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CORROSION OF AUSTENITIC STAINLESS STEEL ALLOYS DUE TO HNO_3-HF MIXTURES

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Chemical Separations Processes
for Plutonium and Uranium
TID-4500

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By
H. S. Cole

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ABSTRACT

This report represents a literature survey, plus some experimental work, on the corrosion of austenitic stainless steel alloys due to HNO_3-HF mixtures. Most of the available data were obtained during the processing of spent nuclear fuel elements where solutions containing nitrates and fluorides are frequently encountered. Austenitic stainless steels have been extensively used in nitrate-fluoride solution service in these plants. It has been shown that their service may be improved by: (1) proper annealing; (2) stabilizing with columbium (niobium) or titanium; (3) complexing the solutions the stainless steels will contain with aluminum, zirconium, or thorium; (4) utilizing stainless steels which have a low carbon content; (5) maintaining the uncomplexed hydrofluoric acid in the solution at as low a value as practicable; and (6) utilizing neutron absorbing elements in the alloys at concentrations as low as possible for service as fixed nuclear poisons. Other protective measures such as reduced contact time, temperature, concentration, and fluoride-to-nitrate ratio can be employed to minimize corrosion.

SUMMARY

Both past and future processes at the Idaho Chemical Processing Plant (ICPP) require the use of corrosive solutions containing nitrates and fluorides for the processing of spent nuclear fuel elements to recover unfissioned uranium-235. By far the most prevalent materials used for process vessels and piping to contain the process solutions have been the austenitic stainless steels. This report summarizes all information available in the literature, both experimental and operational (it also includes some locally obtained experimental results), on the various parameters surrounding the corrosion of austenitic stainless steels by HNO_3-HF mixtures. It discloses that:

(1) Type 304L stainless steel appears to be a suitable choice for service at the ICPP with fully complexed nitrate-fluoride bearing solutions.

(2) Annealing of stainless steels will improve their corrosion resistance.

(3) Stabilizing the stainless steels with columbium (niobium) or titanium will improve their corrosion resistance.

(4) Stainless steels with low carbon content have increased corrosion resistance.

(5) Where it is necessary to alloy neutron absorbing elements in the metal for criticality control purposes, their percentage should be kept to a minimum, as the corrosion rate increases with the increasing addition.

(6) Complexing nitrate-fluoride-containing solutions with aluminum, zirconium, or thorium will also mitigate corrosive effects.

(7) The corrosion of several stainless steel alloys appears to vary directly with the quantity of uncomplexed hydrofluoric acid present.

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I. INTRODUCTION

At the Idaho Chemical Processing Plant (ICPP) located at the Idaho National Engineering Laboratory, spent nuclear reactor fuel elements are processed for the recovery of unfissioned uranium-235. This processing involves the chemical dissolution of the fuel element followed by solvent extraction of the uranium from the dissolver product. Due to the nature of the structure or cladding of the fuel elements, very corrosive mixtures of HNO_3-HF may be required for the dissolution. Naturally it is desirable to construct the dissolver vessel, as well as other vessels and associated piping, of materials which will not also be attacked by these very corrosive dissolver solutions. Some stainless steels have been found to have good serviceability.

Due to the large concentrations of uranium in the solutions being processed it is necessary to include in the system means to prevent nuclear criticality. One such method is the use of nuclear poisons (elements such as boron, gadolinium, cadmium, etc., with a high neutron absorption cross-section) which can be alloyed into the stainless steel structure. However, it has been found that as the percentage of nuclear poisons alloyed into the steel increases, the corrosion resistance of the steel decreases.

The purpose of this work was to evaluate published accounts of the effect of HNO_3-HF mixtures on several stainless steel alloys and present the results of some studies on Type 304 stainless steel modified to contain nuclear poisons. Other alloys such as Inconel, Corronel and the Hastelloys, while possessing potential merit in nitrate-fluoride service, have not been considered in this report.

II. AUSTENITIC STAINLESS STEELS

1. Types and Purposes of Austenitic Stainless Steels

The types of austenitic stainless steels considered in this report are shown in Table I together with their nominal chemical compositions. Also listed are three compositions of Type 304 stainless steel modified to contain boron or gadolinium nuclear poisons.

The chromium-nickel austenitic stainless steels enjoy the greatest usage of all the stainless steels in chemical plant work. They have a low yield strength, excellent ductility and relatively high ultimate tensile strength at room temperature; also, in general, they provide high resistance to corrosion. They are well-suited to standard fabrication methods, having the ductility required for deep drawing and forming[1]. In general their weldability is good, though this will be discussed further. Type 304 ss is the most common grade of the austenitic chromium nickel-alloy steels which are used for handling the most corrosive materials or resisting very severe oxidation. It also possesses high creep strength and may be used at temperatures up to 815°C. However, exposures in the temperature range 425-815°C cause the precipitation of carbides intergranularly and make the material susceptible to intergranular corrosion by certain liquids. Annealed Type 304 ss exhibits excellent corrosion resistance to nitric acid of all concentrations at room temperature and also to boiling acids

TABLE I
TYPES OF STAINLESS STEEL CONSIDERED OR EVALUATED IN THIS REPORT

	Percent Chemical Composition													
Alloy Type	C max	Mn max	P max	S max	Si max	Cr	Ni	Fe	Ti	Cb	Mo	B	Gd	Cu
304	0.08	2.00	0.045	0.03	1.00	18-20	8-12	balance						
304L	0.03	2.00	0.045	0.03	1.00	18-20	8-12	balance						
309	0.20	2.00	0.045	0.03	1.00	22-24	12-15	balance						
309SCb	0.20	2.00	0.045	0.03	1.00	22-24	12-15	balance		10xC				
310	0.25	2.00	0.045	0.03	1.50	24-26	19-22	balance						
316	0.08	2.00	0.045	0.03	1.00	16-18	10-14	balance			2.0-3.0			
321	0.08	2.00	0.045	0.03	1.00	17-19	9-12	balance	0.60 max					
347	0.08	2.00	0.045	0.03	1.00	17-19	9-13	balance		1.00				
Carpenter 20Cb	0.07	2.00	0.035	0.035	1.00	19-21	30-38	balance		1.00 max	2.0-3.0			3.0-4.0
CERTIFIED ANALYSES OF ALLOYS USED IN THIS CORROSION STUDY														
304	0.08	1.78	0.013	0.006	0.59	18.06	13.73	balance				1.48		
304	0.044	1.77	0.006	0.004	0.41	17.69	16.65	balance			<0.01	0.29		
304L	0.03	1.24	0.002	0.001	0.54	18.77	10.82	balance					0.28	
304L*	0.024	1.55	0.021	0.007	0.70	18.03	9.22	balance			0.30			

*welded with 308L wire

up to 50% strength[2]. The corrosion resistance decreases as the concentration and temperatures are increased. Good quality Type 304L ss, in annealed or sensitized condition, exhibits corrosion resistance comparable to that shown for Type 304 ss in the annealed condition. Type 309 ss has a higher chromium and nickel alloy content which improves its corrosion resistance and increases its oxidation resistance up to 1100°C. Its creep strength is slightly better than that of Type 304 ss but less than that of Type 316 ss. Annealed Type 304 ss and annealed or sensitized Type 309SCb ss (stabilized with columbium) have slightly better resistance than annealed Type 304 ss, especially in strong, hot acid. The much higher chromium and nickel alloy content of Type 310 ss enables its use for extreme conditions of corrosion and oxidation. In high temperature service Type 316 ss is very similar to Type 304 ss except that the molybdenum addition greatly enhances its creep strength at all useful temperatures. Types 321 ss and 347 ss in the annealed condition have rates comparable to annealed Type 304 ss. In the sensitized condition they are usually inferior to annealed Type 304 ss or to sensitized Type 304L ss, if the stabilizing elements fail to prevent precipitation of chromium carbides due to improper heat treatment. There is little reason to use Type 321 ss or Type 347 ss for situations involving nitric acid corrosion when annealed Type 304 ss or annealed or sensitized Type 304L ss are available[2].

Not long after the austenitic chromium-nickel steels were first introduced commercially, it was discovered that steels containing about 0.06% carbon became susceptible to severe attack by certain corrosive media in the zones adjacent to the welds when heated to temperatures between 650 and 870°C. This attack, often referred to as weld decay, is associated with intergranular carbide precipitation and is a special case of sensitization[3].

Annealing weldments at high temperatures to redissolve the precipitated carbides will correct this condition. Such treatment, however, is often impractical for large welded vessels. For these conditions the so-called "stabilized" alloys were developed. Many elements such as molybdenum, tungsten, vanadium, columbium (niobium), and titanium were tried but only the last two came into prominent use[4]. Steels with reduced carbon contents were also developed; such steels carry the suffix "L" for low-carbon (or "ELC" for extra low carbon).

2. Purpose of Neutron Absorbers in Stainless Steel

In a plant such as the Idaho Chemical Processing Plant (ICPP), where solutions containing large quantities of fissionable materials are processed, it is necessary to include in the plant processes methods to preserve nuclear criticality safety. These methods include: (1) limits on mass and concentration, (2) limits on geometry, and (3) neutron poisons. Neutron poisons are materials, such as gadolinium, cadmium, or boron, which have a high neutron absorption cross section. Some of the vessels and related process equipment at the ICPP have inserts constructed of Type 304 stainless steel containing 1.5% natural boron. Unfortunately, the boron also reduces the corrosion resistance of the stainless steel; therefore, it is desirable to keep its concentration as low as practicable. Natural boron consists of 19.8% boron-10 and 80.2% boron-11; the boron-10's cross-section is 3.84×10^3 barns while that for boron-11 is 5 millibarns; therefore boron-10 is the effective component.

By alloying the stainless steel with boron-10 rather than natural boron, a reduction to 0.3% boron would still give the same neutron absorption capacity and also improve the corrosion resistance. Neutron poisoning with fixed poisons can be achieved by using other high cross-section elements to alloy with the steel such as cadmium (cross-section equal to 2.45 x 10^3b) or gadolinium (cross-section equal to 4.9 x 10^4b). Thus, both 0.3% and 1.5% boron-alloyed stainless steel and 0.3% Gd alloyed stainless steel were evaluated at ICPP to compare their corrosion characteristics.

III. HISTORICAL (LITERATURE SEARCH)

The use of 10% HNO_3 - 3% HF solutions at 70-80°C for the appraisal of annealed stainless steels has been practiced for some time[5]. This is because it is more effective than any other test for revealing the susceptibility to intergranular attack of the heat-affected zones around the welds. The corrosion is normally evaluated by appearance, including microscopic examination, and weight loss. The test also produces variable but general attack on the annealed stainless steel and it requires care and specialized equipment to perform[5].

In the past a great deal of work has been done on the corrosiveness of HNO_3 - HF mixtures to various stainless steel alloys. A literature search showed that alloys have been tested under variables such as: (1) nitric acid concentration, (2) HNO_3 to HF ratio, (3) temperature, (4) exposure periods, (5) preliminary annealing. There was very little duplication of effort by the various investigators as each had a particular application in mind. While standard methods of corrosion testing do exist, many investigators have preferred to modify them to their own requirements and have reported results obtained over a wide range of exposure conditions. This makes any correlation of the corrosion values reported most difficult.

1. Types of Corrosive Attack

1.1 Intergranular Attack Manifested as Weld Etch

Intergranular attack, working inward between the grains, causes considerably more loss of strength than the same total destruction of metal uniformly distributed over the whole surface; thus there is a risk that, after a long period of corrosion, a member made of material subject to preferential intergranular attack may fail when suddenly subjected to a load which originally it would have been well able to withstand[6].

When an austenitic stainless steel which has been annealed at 500-800°C is immersed in a corrosive liquid, preferential attack along the grain boundaries occurs and stainless steel grains may ultimately be dislodged; given time, the material may even disintegrate to a powder[1]. Weld etch occurs when the metal in the area adjacent to the weld becomes unstabilized due to the heat of welding and thus susceptible to corrosion. One commonly accepted theory as to how the loss of stability takes place is that the alloyed chromium has a high affinity for carbon at high temperatures and separates as particles of chromium carbide along the grain boundaries. Consequently, after welding there is a zone impoverished

in chromium adjacent to the weld. As chromium provides the protective film in stainless steels, an area is exposed which is susceptible to corrosion. There are three methods for combating this type of corrosion: (1) add niobium (columbium) or tantalum to the alloy to act as a stabilizer, since both have an even higher affinity for carbon than the chromium, (2) reduce the amount of carbon in the alloy, or (3) heat treat after welding, followed by quenching, which is designed to bring all chromium carbide back into solution.

When columbium carbide stabilized alloys are welded by two passes, the columbium carbide may be taken completely into solution on the first pass[7]. On the second pass at 482-816°C the $Cr_{23}C_6$, as explained before, is precipitated at the grain boundaries, since chromium diffuses more readily than columbium in this temperature range. Corrosive attack then occurs at areas depleted in chromium.

Kawasaki, Hishinuma and Nagasaki studied the behavior of boron in stainless steel using the ^{10}B (n,α) ^{7}Li reaction[8]. Utilizing a track-etching technique they found that boron atoms segregate easily in austenitic stainless steel grain boundaries upon aging in the temperature range 750 to 850°C. Further, there is a reduction in ductility from irradiation damage due to the (n,α) reaction and above 700°C the helium bubbles which form cause additional mechanical damage. The boron content causes a difference in size and distribution of precipitates such as $Cr_{23}C_6$ in the unstabilized stainless steels, and TiC in the titanium-modified stainless steels, and decreases the solubility of the carbon[8].

Angerman and Kranzlein found that austenitic stainless steels were "sensitized" by heating to temperatures in the range of 425-750°C due to the precipitation of chromium carbides and became susceptible to intergranular corrosion, but they could be stabilized by adding titanium or columbium[9]. In a study of knife-line attack using 3.0*M* HNO_3 - 0.075*M* HF for five 48-hour test periods at boiling it was shown that columbium carbide particles along the grain boundaries were preferentially attacked; when 308L filler rod was used preferential weld corrosion was absent but knife-line corrosion occurred. There was a general attack of the weld metal when the weld filler was the same as the base metal. Therefore, knife-line attack was caused by preferential chemical dissolution of the columbium carbide, which formed a continuous network at grain boundaries in a narrow band between the weld metal and the base metal[9]. They concluded that for Type 309SCb ss there is no way to avoid this; therefore it is not a good candidate for dissolver construction where HNO_3 - HF mixtures will be used.

P. M. Kranzlein compared the corrosion behavior of both wrought and welded Type 304L ss and 309SCb ss in HNO_3 - HF solutions ranging in HNO_3 concentration from 0 - 10.0*M* and HF concentrations from 0.01 - 1.5*M* at temperatures from 24°C to boiling and found that wrought Type 309SCb ss is superior to wrought Type 304L ss[10]. Welds made with Type 309SCb ss filler rod corrode intergranularly at a high rate in boiling solutions of 3.0*M* HNO_3 and 0.075*M* HF. She observed that this intergranular corrosion is due to chemical attack of the columbium carbide particles precipitated in a continuous network throughout the weld. Corrosion resistance of Type 304L ss welded with 308L ss filler is equal to that of wrought Type 304L ss[10].

1.2 Changes in Corrosion Rates with Acid Concentration and Temperature

Besides the weld etch corrosion discussed, there is a general overall attack phenomena due solely to the highly corrosive nature of the HNO_3 - HF system. This attack is intensified with increasing nitric acid concentration, with the HNO_3 to HF ratio, and with temperature. An example is shown in Figure 1[11] which shows an exponential increase in the corrosion rate of Type 304L ss due to these factors.

Occhipinti and Owen, and also Webster, reported on the corrosion of Type 309SCb and 304L ss vessels which were to be used in the dissolution of zirconium alloy fuels[12,13]. It was found that the corrosion rates of both welded and wrought Type 309SCb ss in boiling mixtures of HF - HNO_3 pass through minimum values as the nitric acid concentration is increased from zero up through 0.5*M*, at constant hydrofluoric acid concentration (Figure 2)[13]. In contrast, the rates of corrosion at constant nitric acid concentration increase without minima as the hydrofluoric acid concentration is increased (Figure 3)[13]. Metal-arc welds of Type 309SCb ss are preferentially attacked in boiling mixtures containing nitric acid, although the attack is not pronounced until the concentration exceeds 1.0*M* (Figure 4)[12]. The effect of temperature on the corrosion rate is shown in Figure 5[12]. It was further found that lowering the temperature decreased the corrosion of Type 309SCb ss more than it decreased the dissolution of zirconium. Hence, by keeping the nitric acid concentration below 1.0*M* and the temperatures low (less than 70°C with agitation) the concentration of HF may be increased, by slow continuous addition during dissolution, to give reasonable dissolution rates while the vessel corrosion rate remains low. The slow addition maintained the free fluoride at less than 0.12*M*. Tests showed that the Zircoloy-2 dissolved 4,000 to 6,000 times faster than the stainless steel corroded—a satisfactory rate[12].

The Niflex process (1*M* HNO_3 - 2*M* HF) is used to dissolve Zircoloy or stainless steel clad fuels[10]. Development of this process revealed that HNO_3 - HF was more corrosive than HF alone and caused increased corrosion with increasing concentration and with increasing temperature for the two alloys, Type 309SCb and Type 304L ss (Figures 6 and 7)[10].

1.3 Reducing Corrosion Rates by Postwelding Heat Treatment

Corrosion rates can be moderated through a postwelding heat treatment, as shown for Type 309SCb ss in Table II[7]. In this case columbium carbides are formed in preference to chromium carbides through utilization of the proper times and temperatures, thus the corrosion resistance was improved and the knife-line attack reduced. However, the benefits were not in direct proportion to the heating time, nor was the knife-line attack completely eliminated. As the table shows, however, the treatment for one hour at 1950°F had about the same effect as that for two to ten hours at 1700°F, and the 15-hour hold at 1950°F almost eliminated the knife-line attack[7].

Tests performed by Binder and Brown in a solution containing 10% HNO_3 - 3% HF at 70°C over five 1-hour periods with fresh solution used each period gave the results shown in

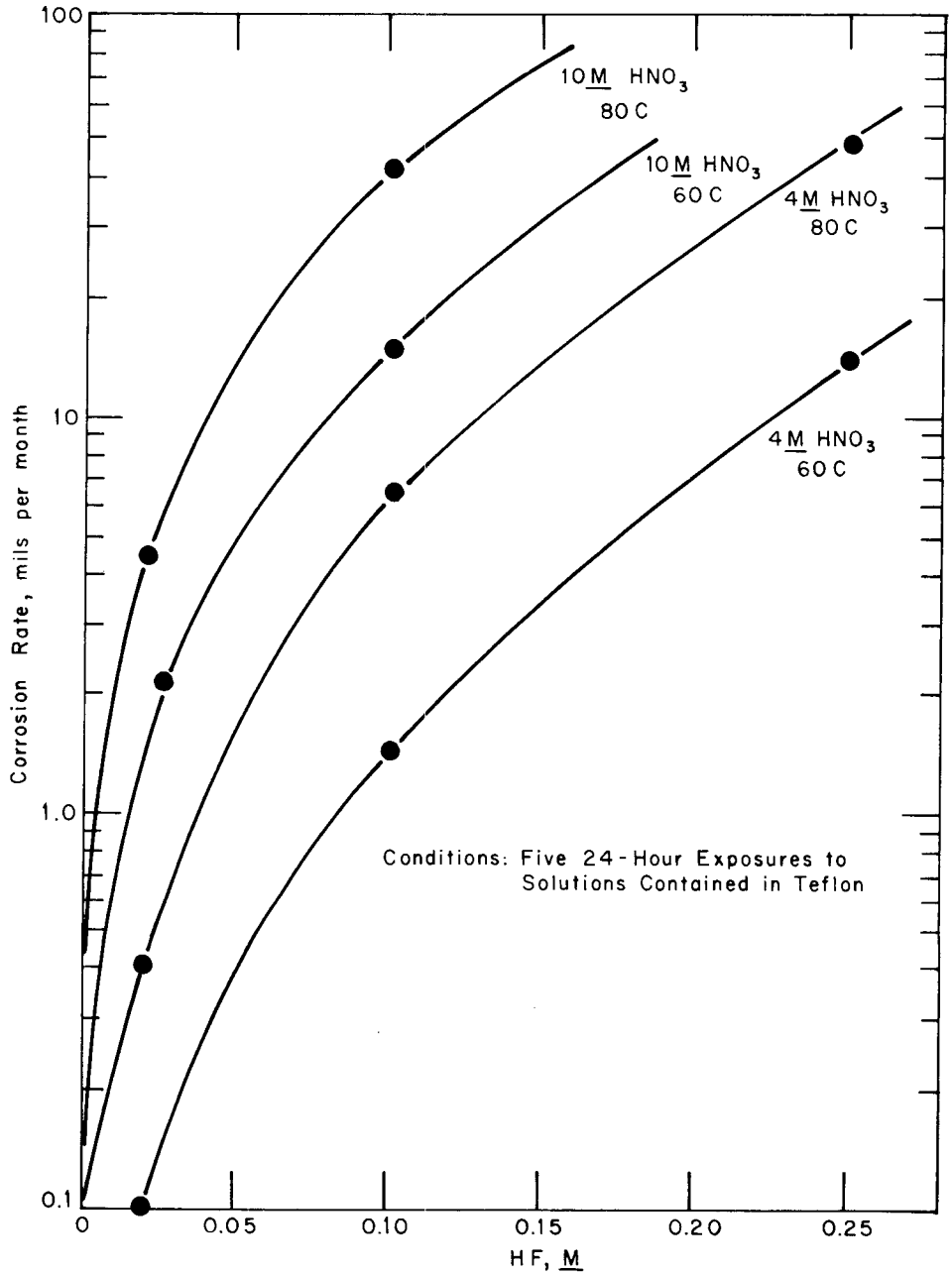

Fig. 1. Type 304L Stainless Steel Corrosion Rates, HNO_3 - HF System[11]

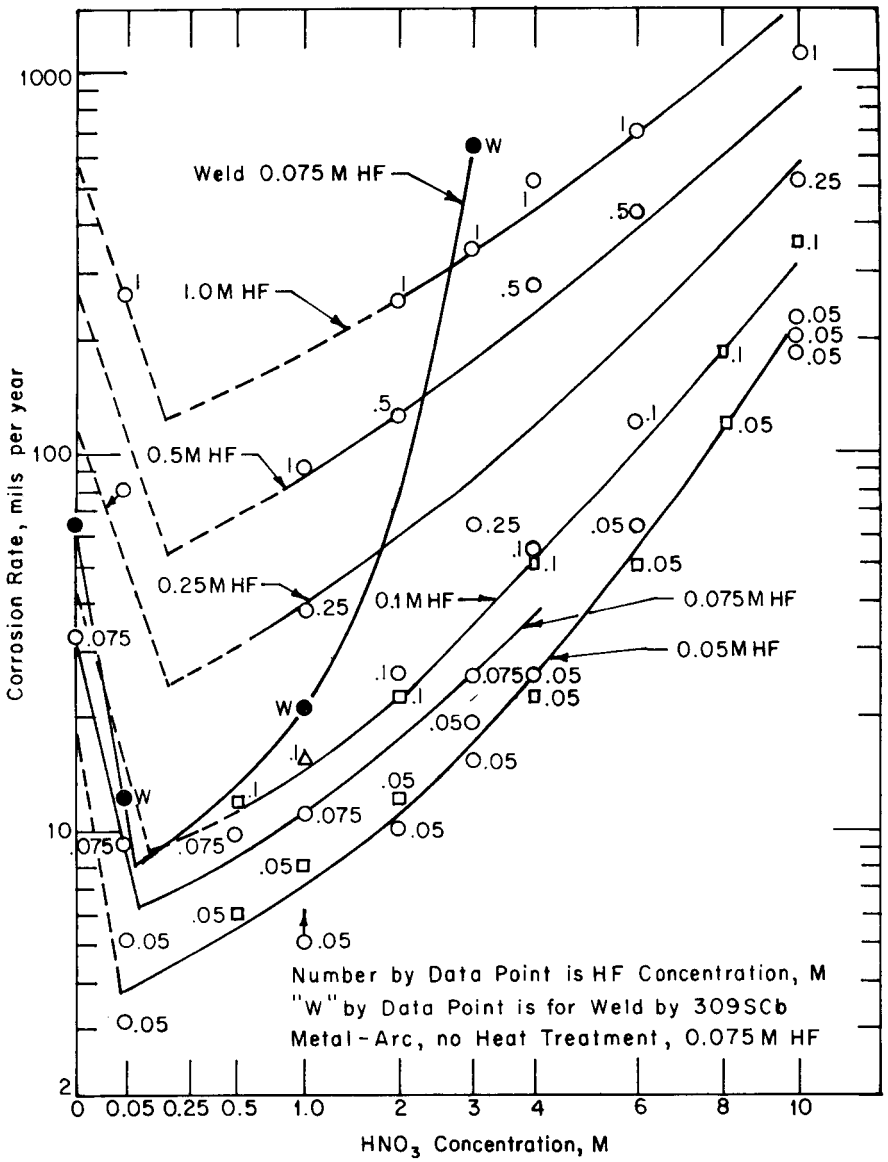

Fig. 2. Corrosion Rate of Type 309SCb Stainless Steel in Boiling HF - HNO_3: HNO_3 Concentration as Continuous Variable[13]

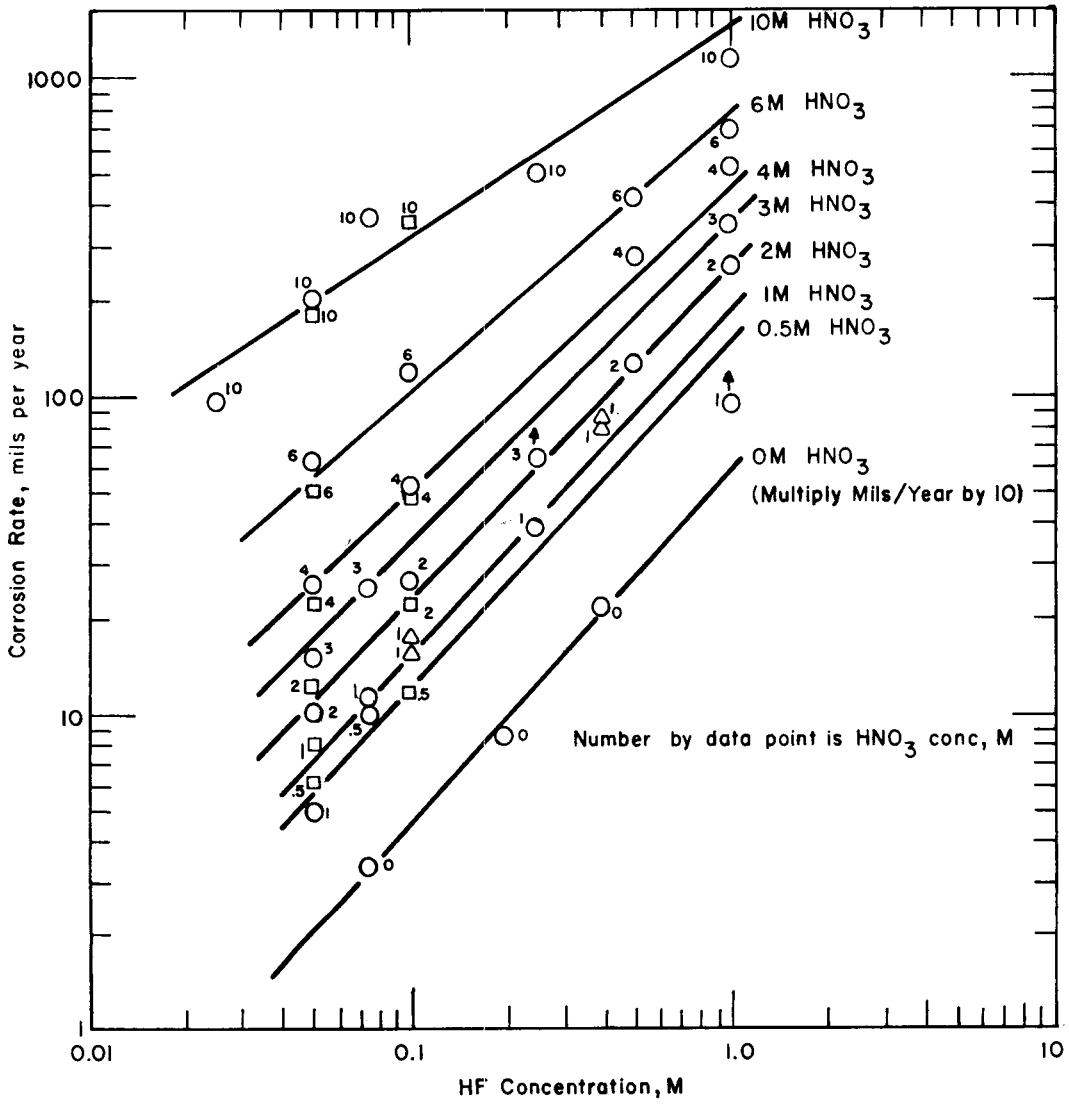

Fig. 3. Corrosion Rate of Type 309SCb Stainless Steel in Boiling HF - HNO_3: HF Concentration as Continuous Variable [13]

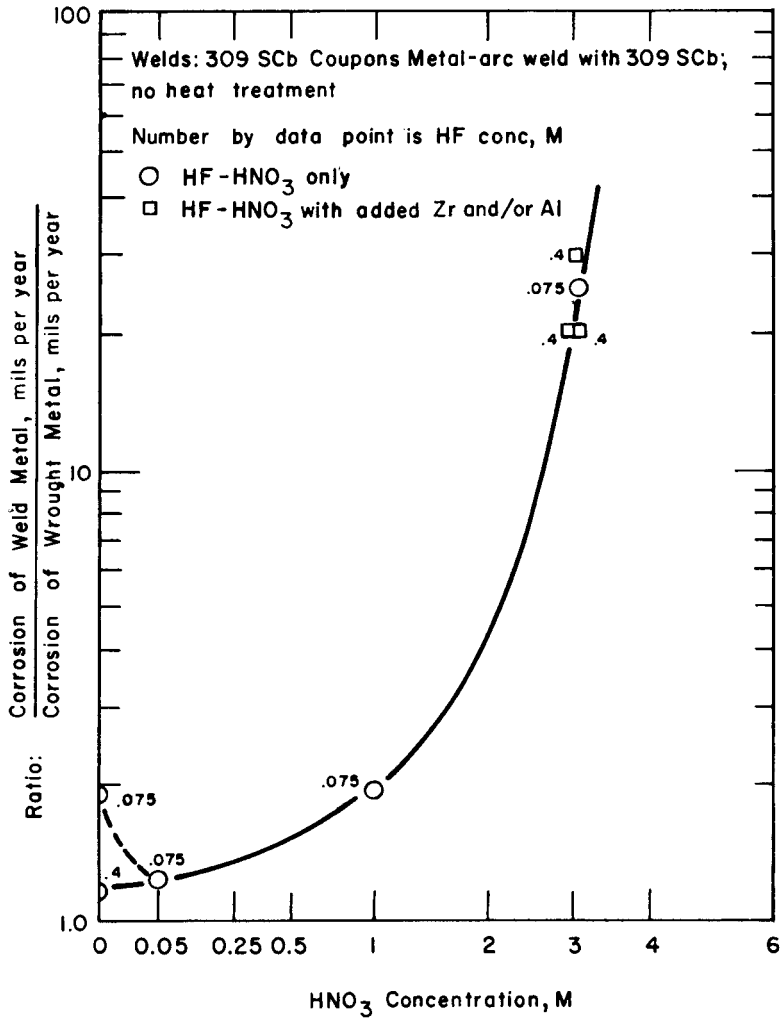

Fig. 4. Increase in Corrosion of Type 309SCb Stainless Steel Welds Relative to Wrought Metal[12]

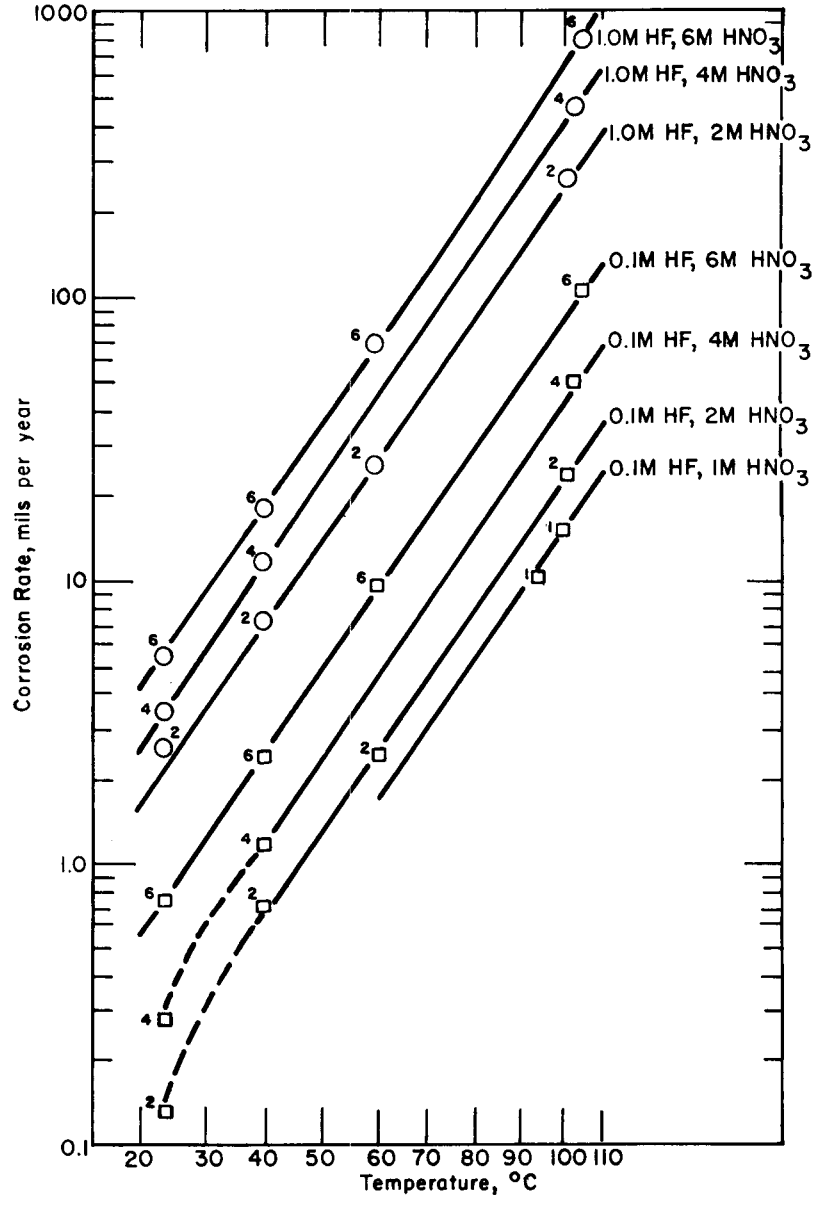

Fig. 5. Corrosion Rate of Type 309SCb Stainless Steel in HF - HNO_3: Temperature as Continuous Variable[12]

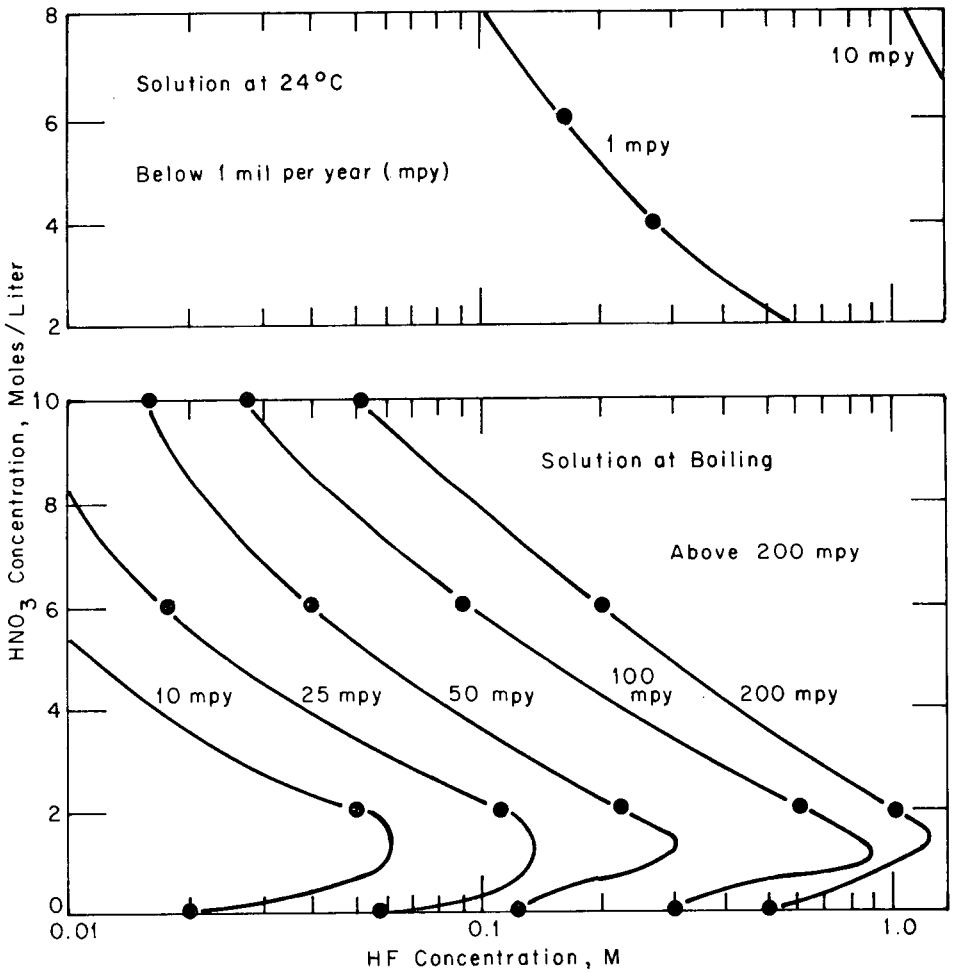

Fig. 6. Corrosion of Type 309SCb Stainless Steel in HF - HNO_3 Solutions[10]

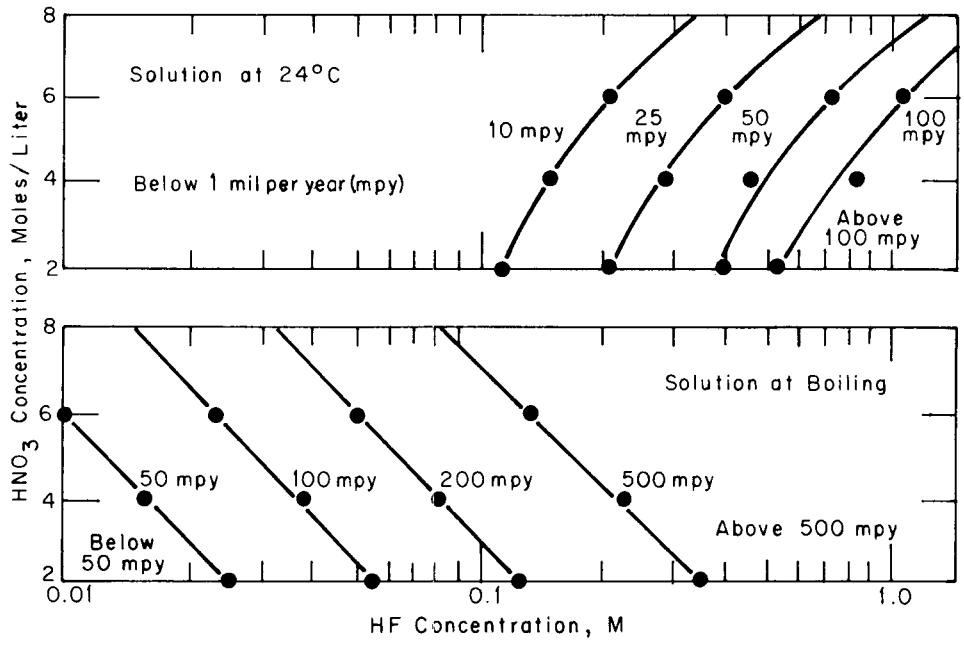

Fig. 7. Corrosion of Type 304L Stainless Steel in HF - HNO_3 Solutions[10]

TABLE II
CORROSION OF WELDED TYPE 309 SCb STAINLESS STEEL COUPONS EXPOSED TO A BOILING SOLUTION OF 13*M* HNO_3 - 0.1*M* HF FOR 24 HOURS(7)

Postwelding Heat Treatment Time, hr.	Corrosion Rate mils/month	Knife-Line Attack mils deep
	1700°F Postwelding Heat Treatment	
0	184	17
0	186	--
2	122	6
2	123	5
6	124	9
6	130	9
10	121	5
10	125	5
	1950°F Postwelding Heat Treatment	
1	136	6
1	116	5
15	106	1
15	112	1

Table III[3]. Accelerated attack occurred in the unstabilized 0.06% carbon, austenitic steels after sensitizing, but was absent in the steels containing niobium. It was also absent in the ELC steels whether or not columbium was present. To prove that the attack was intergranular but that the solution did not corrode intergranularly unless damaging carbide precipitation was present, the specimens were bent after testing. Examination showed that only the high carbon specimens cracked. If they were stabilized with columbium or if they were ELC specimens they did not crack. It appears that the increasing attack which occurred in the high carbon steels after heat treatment at 650°, 750° or 870°C is due to carbide precipitation since the effect can be removed by the addition of a strong carbide-forming element like columbium, or by reducing the carbon to 0.03% maximum. Titanium is used in Type 321 ss and performs the same function as the columbium in Type 318 or Type 347 ss[3].

1.4 Stress Corrosion Cracking

There is very little information available on stress corrosion cracking in HNO_3 - HF environments except for the work of Binder and Brown, which was summarized in the preceding paragraph[3]. Also, Zimmerman and Hoffman noted some evidence of stress corrosion in the processing of mixed raffinates from the processing of both aluminum and zirconium fuels[14]. This attack was on Type 304L ss at 55°C.

TABLE III
RESULTS OF CORROSION TESTS IN
10% HNO_3 - 3% HF AT 70°C[3]

Base Metal*	Corrosion Rate, mils/month			
	a	b	c	d
304 (18 - 10)	800	8,000	5,600	2,900
304 ELC (18 - 10)	920	1,400	550	650
316 (18 - 13 - 2)	65	260	730	270
316 ELC (18 - 14 - 2)	70	75	75	72
317 (18 - 15 - 3)	37	200	550	480
317 ELC (18 - 16 - 3)	32	33	32	29
347 (18 - 11 - 0 - .75)	170	160	100	170
347 ELC (18 - 12 - 0 -.42)	240	150	150	150
318 (18 - 13 - 2 - .70)	24	36	25	30
318 ELC (18 - 14 - 2 - .39)	33	31	29	33

a Heated 15 minutes at 1125°C and air-cooled
b Heated 15 minutes at 1125°C, air-cooled to 650°C for 2 hours, then air-cooled
c Heated 15 minutes at 1125°C, air-cooled to 750°C for ½ hour, then air-cooled
d Heated 15 minutes at 1125°C, air-cooled to 870°C for 2 hours, then air-cooled
* Numbers in parentheses refer to compositions in the order: Cr, Ni, Mo, Nb

1.5 Vapor Phase Corrosion

The information on vapor phase corrosion is also rather scanty. The author has observed some vapor phase corrosion on Type 304 ss containing 1.5% boron which will be reported later. Several references suggest that it is directly correlatable with the concentration of free HF.

Occhipinti, *et al*, found that the addition of $Al(NO_3)_3$ to boiling mixtures of HNO_3 - HF, up to a ratio of Al/F = 2, decreased the fluoride volatility, but further increases had little effect[15]. Also, increased concentrations of HNO_3 increased the volatility. These tests were performed on wrought 309SCb-309SCb welded with 309SCb, and on 304L-304L heliarc welded with 308L. They observed also that the corrosion rates of 304L ss and 309SCb ss vary approximately linearly with the concentration of "free" HF. In their solution, which finally contained 0.5*M* Zr, 0.4*M* NO_3 and 2.5*M* F, they found that the Type 309SCb ss which was in the liquid phase had a corrosion rate of 25 - 30 mpy, while that in the vapor phase was 225 - 250 mpy[15].

At the Savannah River Laboratory, rates of corrosion of wrought Type 309SCb ss were measured for solutions of HF, HNO_3 and Zr^{+4} in which the concentration of free fluoride

was maintained constant[16]. This condition was realized during the dissolution of fuel elements containing zirconium by metering in aqueous HF throughout the dissolution. For these tests the HNO_3 was 1.0*M* while free fluoride was maintained at 0.4*M*, assuming that each mole of zirconium complexed four moles of fluoride. The corrosion rates were measured in both the liquid and vapor phase. Vapor phase measurements were made for samples placed in the returning condensate and for samples "shielded" from the condensate. The results are shown in Table IV. As total fluoride increased from 0.4 to 3.0*M* in 1.0*M* HNO_3 with sufficient Zr^{+4} to maintain free fluoride at 0.4*M*, the corrosion rate in the liquid phase remained constant at about 50 mpy. However, in the vapor phase the rate increased from 11 to 123 mpy for shielded samples and from 112 to 282 mpy for the unshielded samples[16].

Newby and Hoffman evaluated the corrosion of some aluminum-zirconium raffinate blends on Type 304L ss[17]. Their data covered extended exposure periods of 2, 6 and 12 months and included corrosion in the vapor phase, at the interface and in the liquid (Table V). Their values were all for solutions containing the two complexants aluminum and zirconium. Additional work they reported was not included because the other solutions contained chromate. All values reported were remarkably low, however, 10^{-3} mpm, and varied directly with the fluoride concentration, with the exposure time, or with the temperature. The vapor phase coupons sustained more corrosion than did those at the interface or in the liquid. This selective attack by the vapor phase was thought to be associated with the evaporation of the hydrofluoric acid from the solution and its condensation on the coupon in the vapor space where the fluoride, even though low in concentration, is completely uncomplexed by the metallic ions[17].

Type 309SCb ss suffered an overall attack of about 0.3 mil/month in 23*M* HNO_3–1*M* HF during exposures of up to 312 hr[18,19]. The heaviest attack was on the specimen exposed at the liquid-vapor interface. In the presence of graphite and dissolved UO_2, Type 309SCb depassivated after 72 hr of exposure and corroded at excessive rates (~28

TABLE IV
CORROSION OF 309SCb STAINLESS STEEL BY BOILING HNO_3 - HF SOLUTION[16]

Solution Composition, *M*			Liquid	Vapor	
HNO_3	HF	Zr^{+4}		Shielded	Unshielded
1.0	0.4	0	77	11	112
1.0	1.0	0.15	52	28	78
1.0	2.0	0.40	57	79	147
1.0	3.0	0.65	43	123	282

TABLE V
CORROSION OF STAINLESS STEEL TYPE 304L IN BLENDED RAFFINATES FROM ZIRCONIUM AND ALUMINUM PROCESSES[17]

Test Solutions in Order of Decreasing Fluoride Concentration	Test Environment	Cumulative Corrosion Rate (10^{-3} mpm) 2 Mo.	6 Mo.	12 Mo.	Micro-Examination
0.68*M* Zr, 0.68*M* Al	vapor	9.3	9.3	8.0	weld etch
3.51*M* F, 3.53*M* NO_3	interface	4.3	7.8	7.0	knife-line
at 35°C	liquid	4.0	6.8	7.0	weld etch
0.46*M* Zr, 1.04*M* Al	vapor	<0.1	2.7	3.0	etch edges
2.34*M* F, 3.80*M* NO_3	interface	<0.1	2.2	2.0	feebly laminated edges
at 35°C	liquid	<0.1	1.2	1.0	feebly laminated edges
0.08*M* Zr, 1.63*M* Al	vapor	0.1	<0.1	0.4	resistant
0.39*M* F, 5.93*M* NO_3	interface	0.4	<0.1	0.4	resistant
at 35°C	liquid	0.1	<0.1	0.2	resistant
0.08*M* Zr, 1.63*M* Al	vapor	0.4	2.1	3.0	resistant
0.39*M* F, 5.93*M* NO_3	interface	0.5	1.8	2.0	resistant
at 55°C	liquid	0.4	1.3	1.0	resistant

mils/month) in a pitting type of attack. Types 304L and 347 ss corroded at moderate rates ($\leq$5 mils/month) in 22*M* HNO_3–1*M* HF (Table VI)[18,19].

Zimmerman and Hoffman reported on the corrosion evaluation of equipment used for reprocessing zirconium alloy nuclear fuels[14]. This equipment was constructed of Type 304L ss with a portion of the steel plates containing 1.5% boron for criticality control. After 14,568 hours of exposure it was estimated the boron-containing stainless steel plates had lost 1.0 mil of metal from each exposed surface, while the Type 304L ss in the vessel walls had lost an estimated 0.02 mil. Laboratory tests on vapor phase corrosion (shown in Table VII) of Type 304L ss containing 1.5% boron indicate that solutions containing no fluoride or containing 0.1*M* fluoride along with aluminum do not result in excessive corrosion, but significant corrosion is indicated for solutions containing 0.1*M* uncomplexed fluoride. Additional laboratory studies indicated that Types 347, 348, 316, 304L ss in the extraction and waste storage systems will not undergo any significant corrosion at 35°C or less[14].

In the Thorex process, solutions containing 10-13*M* HNO_3 and 0.04 - 0.33*M* HF are used to dissolve thorium fuels. The corrosion rates of those metals exposed in various parts of the Oak Ridge Thorex plant are shown in Table VIII. Corrosion rates were highest in the vapor presumably because of the free HF. The maximum corrosion rate observed was 98 mpy[20,21].

TABLE VI

CORROSION (in mils/month) OF TYPES 304L, 309SCb, AND 347 STAINLESS STEEL IN BOILING 22 to 23*M* HNO_3–1 to 2*M* HF[18,19]

Test Period (hr)	Concentration (*M*) HNO_3	HF	304L V[a]	304L I[a]	304L S[a]	309SCb V[a]	309SCb I[a]	309SCb S[a]	347 V[a]	347 I[a]	347 S[a]
24[b]	22	1	0.1	1.3	4.3				0.1	1.3	4.9
48			0.1	1.4	3.9				0.1	1.3	4.6
24	22	2							<0.1	0.4	0.4
48									0.2	0.5	0.5
72									0.1	0.5	0.5
96									0.1	0.5	0.5
24	23	1				<0.1,<0.1	0.6, 0.6	0.2, 0.3			
48						<0.1,<0.1	0.7, 0.8	0.4, 0.4			
96						<0.1,<0.1	0.6, 0.7	0.2, 0.3			
144						<0.1,<0.1	0.4, 0.6	0.2, 0.3			
192						<0.1,<0.1	0.3, 0.4	0.1, 0.2			
216						<0.1,<0.1	0.3, 0.4	0.1, 0.2			
312						<0.1,<0.1	0.2, 0.3	0.1, 0.2			
96	23	1				<0.1,<0.1	1.1, 0.2	15.7, 24.7[c]			

[a]V - in vapor phase; I - at the vapor-liquid interface; S - in solution.

[b]These solutions contained 50 g of dissolved uranium and 20 g of solid graphite per liter.

[c]Pitting occurred.

TABLE VII
VAPOR PHASE CORROSION OF TYPE 304L STAINLESS STEEL CONTAINING 1.5 PERCENT BORON[14]

Test Solution Composition:		Solution 1	Solution 2	Solution 3
U	*M*	0.84	0.84	0.84
NO_3	*M*	3.78	3.78	4.68
H	*M*	2.1	2.2	2.2
F	*M*	---	0.1	0.1
Al	*M*	---	---	0.3
Corrosion Rates (MPM) Following Individual Exposure Periods				
24 hours @ 85 C		---	0.8[a]	0.2[a]
23 hours @ b.p.		0.16	8.6[a]	0.11
90 hours @ b.p.		0.30	8.6	0.32

[a] Results of a single determination—other results represent the average of two determinations.

TABLE VIII
SUMMARY OF CORROSION RATES FOR STAINLESS STEELS EXPOSED IN ORNL THOREX PLANT[21]

Period of Operation	Process Vessel	Operating Temperature C	Specimen Location	Exposure Time, hr	Corrosion Rate, mils/yr 304L	309SCb
Development	Batch dissolver tank	110-115	Solution	2706	31.8 ± 0.9	15.0 ± 1.6
			Vapor	2706	40.3 ± 1.5	34.9 ± 1.9
Development	Feed adjustment tank	110-115	Solution	2609	(a)	41.4 ± 4.8
			Vapor	2609	97.5 ± 2.5	85
Development	BT vapor separator	115	Vapor	5788	54.5	25.4 ± 4.7(b)
Development	A-column feed tank	30-60	Solution	7307	<0.1	<0.1(b)
Development	BTC catch tank	15-30	Solution	5135	<0.1	<0.1(b)
Production-development	Batch dissolver tank	110-115	Solution	3340	25.4 ± 2.4	16.4 ± 0.2
			Vapor	3340	53.7 ± 0.5	41.8 ± 1.9
Production-development	BT vapor separator	115	Vapor	6698	30.1	107 ± 43(c)

(a) Specimen lost.
(b) Rates are for 347 stainless steel.
(c) Composite rates for 309SCb and 347 stainless steels.

2. Stainless Steel Alloys Evaluated in HNO_3 - HF Solutions

As mentioned initially, this investigation was restricted to the corrosion of certain specified stainless steel alloys in HNO_3 - HF solutions.

A series of tests performed by Bloom and Carruthers using a solution containing 10% HNO_3 - 3% HF at 80°C with exposures of three 4-hour periods and fresh acid used for each period gave the results shown in Table IX[22]. It may be noted that the corrosion rates were the lowest on those steels with the highest nickel content and that the columbium stabilized and ELC (extra low carbon) specimens showed no heat-affected zone (knife-line) attack.

The General Electric Company, Hanford Works, encountered difficulties with the use of Type 304L ss in storage tanks, concentrators, and dissolver vessels, particularly when nitric-hydrofluoric mixtures were utilized[23]. They investigated Types 309L ss and 309SCb ss, and, while an improvement over Type 304L ss, they did not fulfill all the desired characteristics needed. Therefore, the Allegheny Ludlum Steel Corporation undertook an investigation of new or improved alloys which might be used in processing equipment, and especially equipment handling nitric-hydrofluoric acid mixtures. Their investigation included the use of boiling 13*M* HNO_3 with additions of 0.075*M*, 0.25*M* and 0.50*M* HF, and they found that much improved general corrosion resistance over Type 309 ss can be obtained with 0.02% carbon Type 310Cb ss, with 0.02% carbon Type 310 ss, and with all of

TABLE IX
RESULTS OF CORROSION TESTS ON WELDED SPECIMENS USING 10% HNO_3 - 3% HF SOLUTION[22]

Base Metal and Composition	Corrosion Rate mil/month	Knife-Line attack
Type 304 (18Cr - 8Ni)	454-487	yes
Type 316 (18Cr - 12 Ni - 3Mo)	157-150	yes
Type 347 (18Cr - 10Ni - +Cb)	114-384	no
Type 304 ELC (18Cr - 8Ni)	351-384	no
Type 347 ELC (18Cr - 10Ni - +Cb)	222-227	no
Type 316 ELC (18Cr - 12Ni - 3Mo)	91-122	no

the high chromium-nickel alloys. Also, 0.02% carbon Type 310 ss had good properties and could be processed to plate or sheet and welded without cracking.

The fifteen different heats utilized, which are shown in Table X, with their compositions, were descaled in 15% HNO_3 - 3% HF before cold rolling[23]. After this they were degreased in a 10% alkaline cleaner and annealed at 2050°F or 2150°F. They were tested in one of three solutions of interest for six 24-hour periods at boiling:

13*M* HNO_3 + 0.075*M* HF
13*M* HNO_3 + 0.25*M* HF
13*M* HNO_3 + 0.50*M* HF

TABLE X
CORROSION OF SPECIAL ALLOYS IN BOILING SOLUTIONS[23]

Item	Percent Composition C	Mn	Si	Cr	Ni	Cb	t°F	13*M* HNO_3 .075*M* HF	13*M* HNO_3 .25*M* HF	13*M* HNO_3 0.5*M* HF
									Corrosion Rate, mpm	
1	.03 max	.75	.35	35	20	--	2050	11	34	37
							2150	12	30	42
2	.03 max	.75	.35	30	20	--	2050	11	32	42
							2150	13	34	--
3	.03 max	.75	.35	30	25	--	2050	10	29	44
							2150	10	26	39
4	.03 max	.75	.35	30	15	--	2050	17	37	51
							2150	18	34	48
5	.03 max	.10	.35	25	20	--	2050	23	61	72
							2150	30	75	98
6	.03 max	.75	.30	25	20	--	2050	15	39	53
							2150	16	43	--
7	.03 max	.75	.00	25	20	--	2050	17	52	62
							2150	18	47	58
8	.03 max	.75	0	25	20	--	2050	17	44	70
							2150	18	49	61
9	.03 max	.75	.15	25	20	--	2050	15	44	75
							2150	17	42	70
10	.03 max	1.50	.40	22¼	14½	--	2050	25	76	104
							2150	23	54	102
11	.01 max	1.50	.40	22¼	14½	--	2050	20	57	93
							2150	21	52	90
12	.005 max	1.50	.40	22¼	14½	--	2050	19	57	87
							2150	19	70	106
13	.01 max	.50	.40	22¼	15¼	--	2050	19	59	85
							2150	18	54	89
14	.05 max	1.50	.40	22½	14½	.50	2050	23	---	126
							2150	21	---	94
15	.02 max	.75	.35	25	20	.20	2050	13	---	64
							2150	13	---	74

Their investigation found slightly decreasing corrosion rates with increases in annealing temperature, but the reverse was true in enough cases to warrant the recommendation that the choice of annealing temperature should be governed by the metal's proposed environment and the structure of the alloy material involved[23]. The high chrome-nickel alloys showed the lowest corrosion rates. The Type 310 ss showed marked improvement over the Type 309 ss, but no improvement in resistance could be found for the low silicon nor for the low manganese. In the Type 309 ss group the very low carbon content did not appear to help. Welded samples showed end-grain attack, weld attack and possible intergranular attack. End-grain attack is a problem with heavy sections where the edge-to-surface area ratio is appreciable. Pitting of the weld surface and ends could have a serious influence on corrosion rate. In Table X Samples 2 and 15 were rated the best[23].

In 1954 Gercke and Lewis at Livermore Research Laboratory reported on the corrosion of several stainless steels in nitric-hydrofluoric acid mixtures[24]. They were looking for a suitable dissolver vessel material, to serve in the dissolution of zirconium-clad fuel elements, that would have a corrosion rate of less than 120 mpy. They investigated Types 309, 309SCb, 304ELC, 316ELC, and 347 ss, and Durimet 20 ss, and obtained the results shown in Table XI. They concluded that only 309SCb ss and Durimet 20 ss gave good corrosion resistance. Several of the alloys gave poor results because of excessive corrosion at the weld. They also felt that if the temperatures had been increased to 110°C probably none of the alloys would have been satisfactory.

Bordeaux and Adams surveyed eight metals for use in the construction of dissolvers, columns, evaporators and piping at the Idaho Chemical Processing Plant for hydrofluoric-nitric acid service[25]. Only three of the eight metals tested were austenitic stainless steels and none were considered suitable for the proposed service. Table XII shows their reported values. The exposed specimens suffered severe grain boundary attack, pitting, laminations and dissolution. The high corrosion rates did not justify exposures longer than the three 48-hour periods given[25].

TABLE XI
THE CORROSION OF SOME STAINLESS STEELS IN 20% HNO_3 - 3% HF[24]

Stainless Steel Type	Temp. °C	Exposure Time, hr.	Penetration, mpy Total Immersion Nonwelded	Total Immersion Welded	50% Immersion Nonwelded	50% Immersion Welded
309	30	92	70	--	54	--
309	57	114	139	154	83	197
309SCb	30	92	62	25	37	26
Durimet 20	30	92	19	--	14	29
Durimet 20	30	138	19	--	15	--
Durimet 20	31	46	19	29	15	27
304ELC	57	114	--	800[a]	1290	--
316ELC	57	114	--	590[a]	810	--
347	57	114	270	312	191	190

(a) 309SCb welds

TABLE XII
CORROSION RATES OF ALLOYS IN BOILING HF - HNO_3[25]

Solution Composition	Metal, mpm corrosion		
	Type 309SCb ss	Type 316 ELC ss	Carpenter-20 SCb ss
10.0*M* HF	516	796	70
8.0*M* HF, 1.0*M* HNO_3	153	452	179
6.0*M* HF	---	---	171
6.0*M* HF, 0.25*M* HNO_3	---	---	106
6.0*M* HF, 6.0*M* HNO_3, 0.5*M* Al^{+3}	119	240	190
3.0*M* HF, 6.0*M* HNO_3, 1.0*M* Al^{+3}	23	45	35
2.0*M* HF, 6.0*M* HNO_3	129	---	248
1.0*M* HF, 13.0*M* HNO_3	36	153	161
1.0*M* HF, 6.0*M* HNO_3	---	---	150

3. Decontamination Using Nitric-Hydrofluoric Acid Mixtures

Hanford Laboratories reported on the use of 20% HNO_3 - 3% HF as a decontaminating solution for Type 304L ss in 1956[26]. Experimentally they sensitized their Type 304L ss specimens by heating them one hour at 1250°F followed by a water quench. They were passivated in 20% HNO_3 prior to exposure. The proposed decontaminating solution was found to be very corrosive with rates approaching 1,000 mpm. They felt the corrosion mechanism was the same at all temperatures but decreased with time (on a short-term basis), and that it would be a good cleaner with judicious selection of time and temperature to minimize the damage[26].

4. Aqueous Wastes Containing Nitrates and Fluorides

The effect of aqueous wastes, which contain nitrates and fluorides from various nuclear fuel reprocessing solutions, on austenitic stainless steel tanks is a special application in this study. Not only are the aqueous waste solutions highly radioactive, but they also contain high concentrations of other anions and cations. For example, a typical first-cycle raffinate from the processing of zirconium-base fuels (aluminum nitrate is added to complex fluoride) may contain 0.52*M* Zr, 2.9*M* F, 0.72*M* Al, 2.0*M* acid, 3.3*M* NO_3, 0.01*M* Cr_2O_7 and 0.007*M* Sn. At 60°C, Types 347 and 316 ss corrode at rates of less than 1 mpm[27]. When neutralized with caustic to pH 10, this solution corrodes welded Types 304L and 347 ss at rates of less than 0.0005 mpm[28]. Mixed raffinates from the processing of both aluminum and zirconium fuels (0.48*M* Zr, 0.62*M* Al, 3.0*M* F, 0.99*M* acid, 1.81*M* NO_3, 0.015*M* CrO_3) attack Types 304L and 347 ss at rates of less than 0.004 mpm at 35°C[17]. At 55°C, the rate of attack is about 0.03 mpm for Type 304L ss; attack is more severe in the vapor, and there is evidence of grain boundary attack and stress corrosion cracking[14].

Type 316L ss is used in some storage tanks at the ICPP to hold the zirconium raffinate. The corrosion behavior of Type 316L ss specimens in this environment is summarized in Table XIII[29,30]. After more than five years exposure, the corrosion rate of the Type

TABLE XIII
CORROSION OF TYPE 316ELC STAINLESS STEELS IN ZIRCONIUM RAFFINATE[29,30]

Type of Specimen	Number of Specimens	Heat Treatment	Exposure Time, days	Maximum Rate, mils/yr
Stressed hoop, 1.25-in. diam. x 0.125-in. wall	1	677°C for 1 hr	48	0.12
American Welding Society ER-316L welding rod used	2	677°C for 1 hr	398	0.04[a]
	1	677°C for 1 hr	449	0.13
	1	677°C for 1 hr	554	0.12
	2	As-welded	849	0.11
	1	As-welded	1855	0.06
Stressed hoop, 2.5-in. diam. x 0.125-in. wall	2	677°C for 1 hr	849	0.08
American Welding Society ER-316L welding rod used	1	677°C for 1 hr	1855	0.08
	1	As-welded	48	0.24
	2	As-welded	398	0.04
	1	As-welded	499	0.15
	1	As-welded	554	0.14
Weld tabs 3 in. x 6 in. x 11/16 in.	2	677°C for 1 hr	1855	0.07
American Welding Society ER-316L (0.06 percent C) welding rod used	2	As-welded	389	0.12

(a) 15-mil-deep pits in weld.

316L ss is less than 0.1 mpy. These specimens exhibit only mild dendritic attack and no pitting. However, pitting to a depth of 15 mils after a 13-month exposure has been observed in one of two 316L ss weld deposit specimens which were sensitized and stressed[29,30].

5. External Means for Corrosion Inhibition

In addition to the various stainless steel alloys developed to resist corrosion, including low-carbon alloys and stabilizers, many investigators have considered additives to

the highly corrosive HNO_3 - HF solutions. These additives have included aluminum, zirconium, thorium and others.

In 1954 Moore and Watts performed a series of experiments to demonstrate the magnitude of fluoride corrosive behavior and to test a number of substances as possible corrosion inhibitors[31]. Their tests were performed using boiling nitric acid containing 0.1*M* HF on Types 309SCb, 347 and 304L ss; very rapid corrosion (300 - 900 mpy) was observed. They found that the presence of 1*M* thorium in the solution would reduce the corrosion to an acceptable level. Of several metal cations which were tested, zirconium produced the best inhibition, reducing the corrosion rate approximately 25-fold. They also tested titanium and vanadium oxides but decided they were too insoluble to give the needed concentration of cations in the solution to inhibit corrosion[31].

In 1959 Kranzlein, Holzworth and Snyder reported on the "Corrosion of Stainless Steel in Thorex Process Solutions"[32]. In the Thorex process, solutions containing 10 - 13*M* HNO_3 and 0.04 - 0.33*M* HF are used to dissolve thorium fuels. It was found that the addition of aluminum ions or the buildup of Th^{+4} ions in the acids reduces the corrosion rate of most materials, presumably by complexing the fluoride ion. This is shown in Table XIV[32,33]. Types 304L and 309SCb ss are used extensively in the Thorex process. Thus they found it was desirable to leave a heel of thorium in the boiling HF - HNO_3 dissolving solution to minimize the high initial corrosion rate of the Type 309 SCb ss. Then, to take care of the Type 304L ss corrosion in the low activity waste evaporator, they added one mole of aluminum per mole of fluoride to the evaporator feed. Their dissolver solutions consisted of 10*M* HNO_3 and 0.05 to 0.10*M* HF which corroded Type 309SCb ss at 205 to 365 mpy. They also found that welds of Type 309SCb ss corroded 20 times faster than the wrought metal. However, if the solution contained 1.0*M* $Th(NO_3)_4$, the corrosion rate was less than 10 mpy. In the instance shown in Table XIV, the addition of 0.09*M* $Th(NO_3)_4$ to boiling 10.3*M* HNO_3 and 0.075*M* HF solution reduced the corrosion rate of Type 309SCb ss from 290 to 37 mpy, and of 304L ss from 390 to 61 mpy. It was found that twice the $Th(NO_3)_4$ concentration needed for wrought metal was required to achieve an equivalent reduction for the weld metal. The corrosion rate for Type 304L ss increased with either an increase in HF or HNO_3 concentration and decreased with an increase in the $Th(NO_3)_4$ concentration[32]. In 60°C solutions, each mole of thorium was able to complex four moles of fluoride. However, in boiling 10*M* HNO_3, at least two moles of thorium per mole of fluoride was required to reduce the corrosion rate of Type 309SCb ss below 25 mpy. Also, a ratio of one mole of $Al(NO_3)_3$ per mole of fluoride was required to reduce the corrosion rate of Type 304L ss to 22 mpy.

Savannah River reported that in the dissolution of thorium utilizing 10*M* HNO_3 plus either 0.05*M* or 0.1*M* HF, when testing the corrosion rate of Types 309SCb or 304L ss, it was found that corrosion of the steel is inhibited by the complexing of the fluoride with thorium[34]. The effect increases with the quantity of thorium dissolved. It was also affected by the initial dissolution of aluminum fuel cans. Welded coupons corroded at about twice the rates of unwelded coupons, but examination showed no obvious localized attack at the welds. Corrosion rates were also twice as fast with the 0.1*M* HF as they were with the 0.05*M* HF.

TABLE XIV
CORROSION OF ALLOYS IN BOILING SIMULATED THOREX SOLUTIONS[32]

Solution Composition, *M*					Alloys–Corrosion Rate, mils/yr							
HF	HNO_3	$Th(NO_3)_4$	$Al(NO_3)_3$	$NaNO_3$	304L	309SCb	309	310	329	347	Carp.20	Tantalum
0.075	10.3	–	–	–	390	290	150	233	452	710	390	22
0.05	10.3	–	–	–	205	143	105	–	–	450	–	–
0.075	10.3	0.09	–	–	61	37	–	30	68	138	49	–
0.075	0.5	2.0	–	–	1.5	1.0	–	–	–	–	–	–
0.009	5.6	–	–	1.47	27	13	–	13	22	38	20	–
0.07	–	–	0.6	–	Nil	Nil	–	Nil	Nil	Nil	Nil	–

In a subsequent work (1960), Kranzlein reported additional corrosion studies utilizing HF concentrations from 0.01 to 1.5*M* on Types 304L and 309SCb ss[10]. While the Al/F = 1 ratio is satisfactory for low fluoride concentrations and temperatures, as the concentration or temperature increases the Al/F ratio must also increase to maintain the same level of corrosion resistance. Table XV summarizes the effect of $Al(NO_3)_3$ on the corrosion of Type 304L ss. Kranzlein also observed that the corrosion rate was highest in the liquid phase and that corrosion increased with temperature. Some work was also done with zirconium metal, uranium, molybdenum, $AgNO_3$, $Fe(NO_3)_3$, and $Ca(NO_3)_2$. The zirconium metal was found to be significantly the best inhibitor. Its corrosion data indicated ZrF_2^{+2} or ZrF_3^{+} was forming rather than ZrF_4, as predicted[10].

Walker, in 1962, went a step further by working with nitric acid concentrations up to ten molar[35]. He found that by using an aluminum-to-fluoride mole ratio of five or six, he could produce almost complete corrosion inhibition in a 0.01*M* HF solution. See Figures 8, 9 and 10.

The National Lead Company of Ohio in a Summary Technical Report reported on the inhibiting effect of inorganic cations toward nitric acid containing fluorides in a system constructed of Type 304L ss[36]. Specifically they studied the amounts of Fe^{+3}, Al^{+3}, or Th^{+4} necessary to hold to a tolerable level (25 mils per year) the corrosion rate of Type 304L ss in nitric acid solutions ranging from 2*M* to 12*M* and containing 0.1*M* HF. The temperatures surveyed ranged from 80°F to 190°F. They found that the corrosion rate depended upon the cation-to-fluoride ratio as well as acid concentration and temperature. Also, they found that Th^{+4} ions have a greater inhibiting effect that Al^{+3} ions at lower acidity, but at higher acidity Al^{+3} ions are more effective in reducing corrosion. Figures 11 and 12 show that an Al/F molar ratio of two is required to reduce the corrosion rate below 20 mpy in 12*M* HNO_3 at 190°F. Figures 13 and 14 show that Th^{+4} additions have greater inhibiting effects than Al^{+3} below 6*M* HNO_3 at all temperatures studied, but at 12*M* HNO_3, Th^{+4} has less inhibiting effect. The corrosion rate can be reduced by the addition of Fe^{+3}

TABLE XV
SUMMARY OF HNO_3 - HF - Al CORROSION DATA (TYPE 304L STAINLESS STEEL AT 24°C)[10]

Solution Composition, *M*			Corrosion Rate
HNO_3	HF	$Al(NO_3)_3$	mpy
2.0	0.5	0.1	36
2.0	0.5	0.25	4.9
2.0	0.5	0.5	0.12
2.0	1.5	0.1	170
2.0	1.5	0.25	81
2.0	1.5	0.5	17
2.0	1.5	0.75	0.8
4.0	1.0	0.1	51
4.0	1.0	0.25	38
4.0	1.0	0.5	1.7
4.0	1.5	0.25	95
4.0	1.5	0.5	9.0
4.0	1.5	0.75	1.3
6.0	1.0	0.1	39
6.0	1.0	0.25	31
6.0	1.0	0.50	2.5
6.0	1.5	0.1	88
6.0	1.5	0.25	71
6.0	1.5	0.5	3.6

only at low HNO_3 concentrations and low temperatures; at higher conditions its effect is negligible[36].

The Dow Chemical Company reported on an 18-inch diameter ion exchange column constructed of Type 304L ss containing 1% boron-10 which was used for the recovery of plutonium from streams containing 7*M* HNO_3 - 0.1*M* HF[37]. Tests were run to ascertain that the alloy would not corrode at a rate which would create problems in nuclear safety, as the boron was present to serve as a nuclear poison. The tests indicated that the metal was satisfactory for use with the above solution when the free fluoride had been complexed with 2.5:1 atom ratio of aluminum ion. However, substantial corrosion rates were observed if the aluminum ion complexant was not used. Also, it was found that the corrosion rate increased one and one-half times for each 10°C increase in temperature[37].

In the Niflex process (mentioned previously in III.1.2) which is used to dissolve zirconium alloy or stainless steel clad fuels[38], it was found that the addition of 0.3*M* aluminum ion to boiling 4*M* HNO_3 - 0.6*M* HF reduces the rate of attack on Type 304L ss from 250 mpm to 30 mpm and that on Type 309SCb ss from 30 to 5 mpm. Tetravalent zirconium also complexes fluoride ions and reduces corrosion attack[38]. See Table XVI.

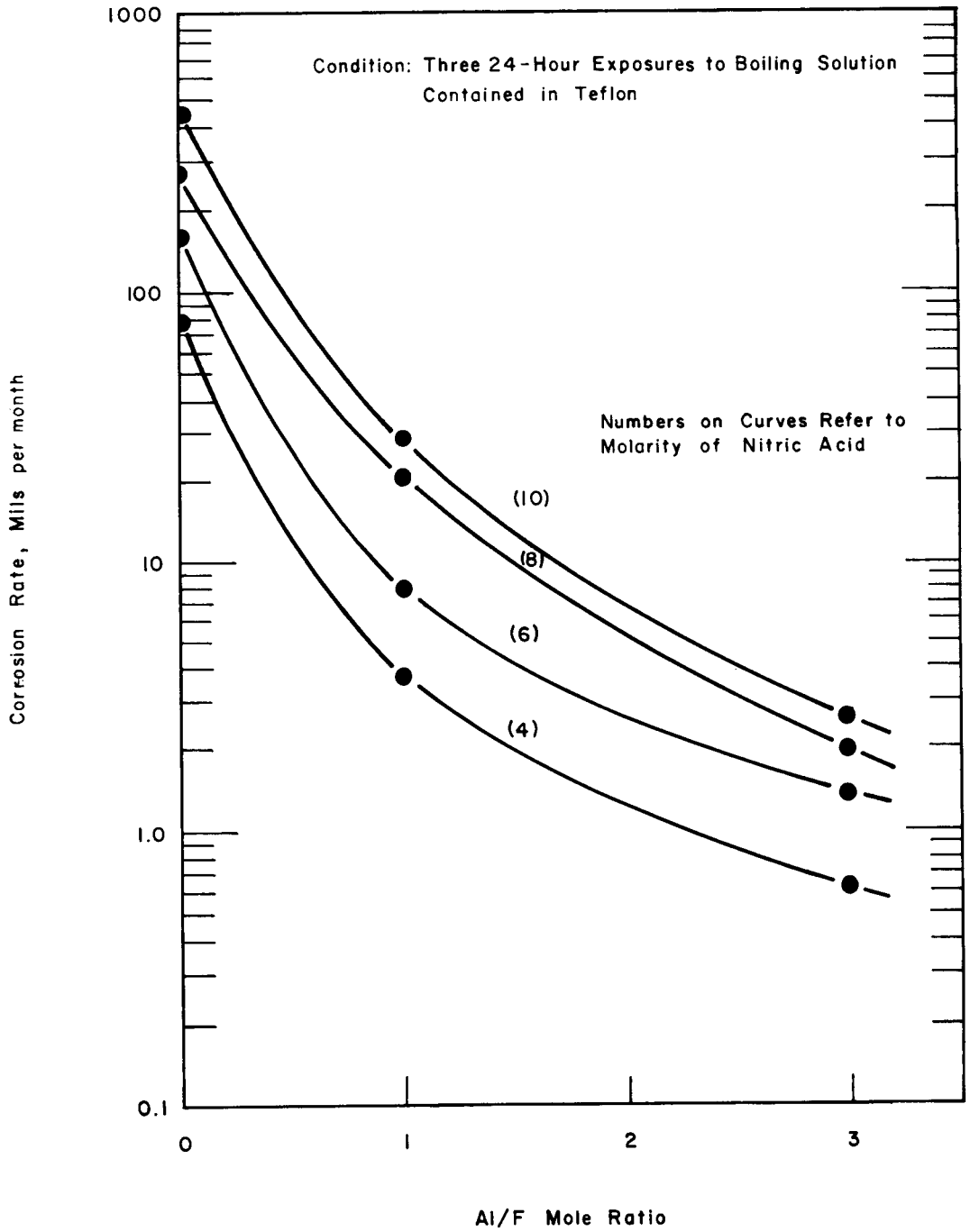

Fig. 8. Type 304L Corrosion Rates, 0.25*M* HF - HNO_3 - $Al(NO_3)_3$ System[35]

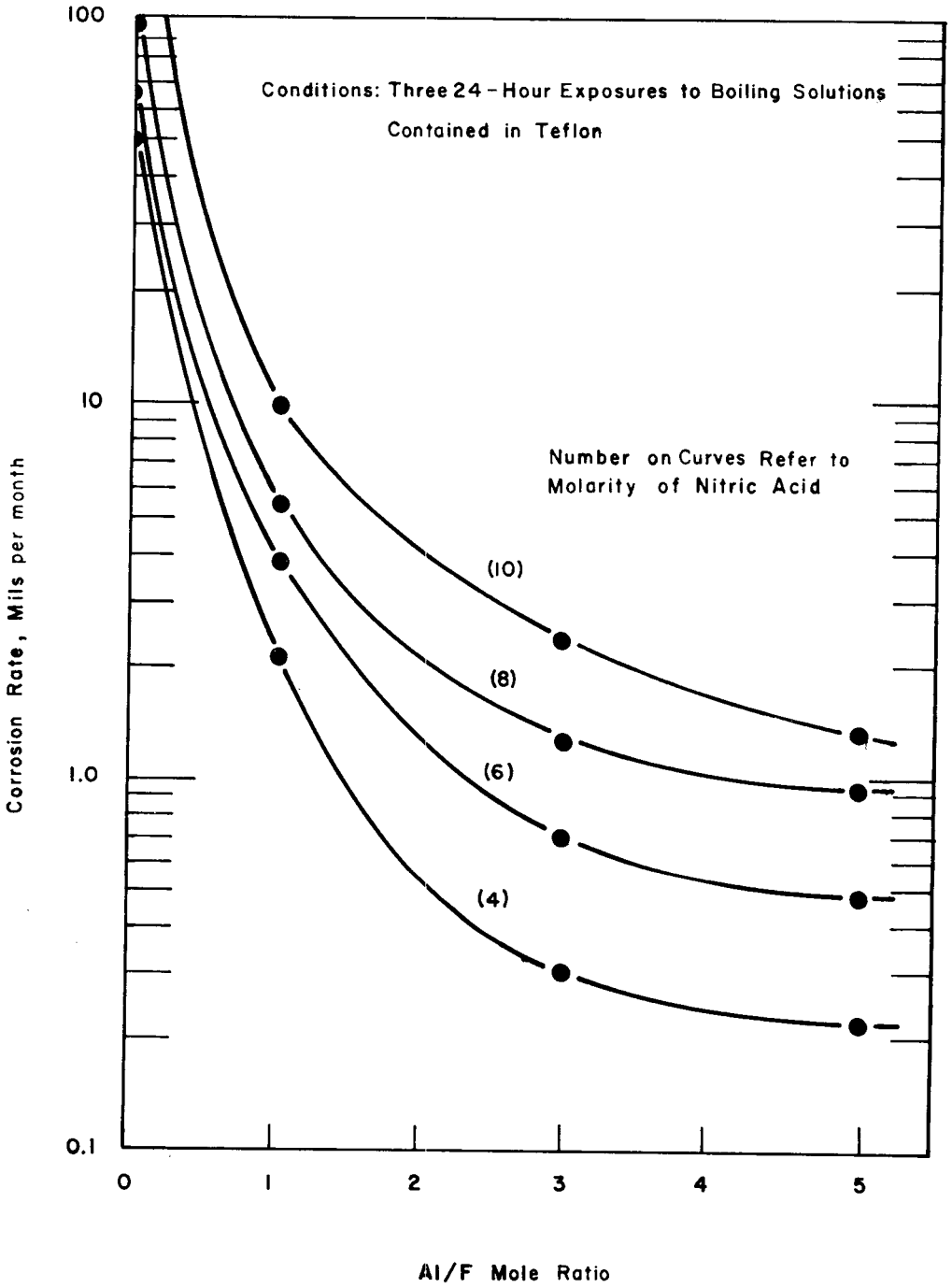

Fig. 9. Type 304L Corrosion Rates, 0.1*M* HF - HNO_3 - $Al(NO_3)_3$ System[35]

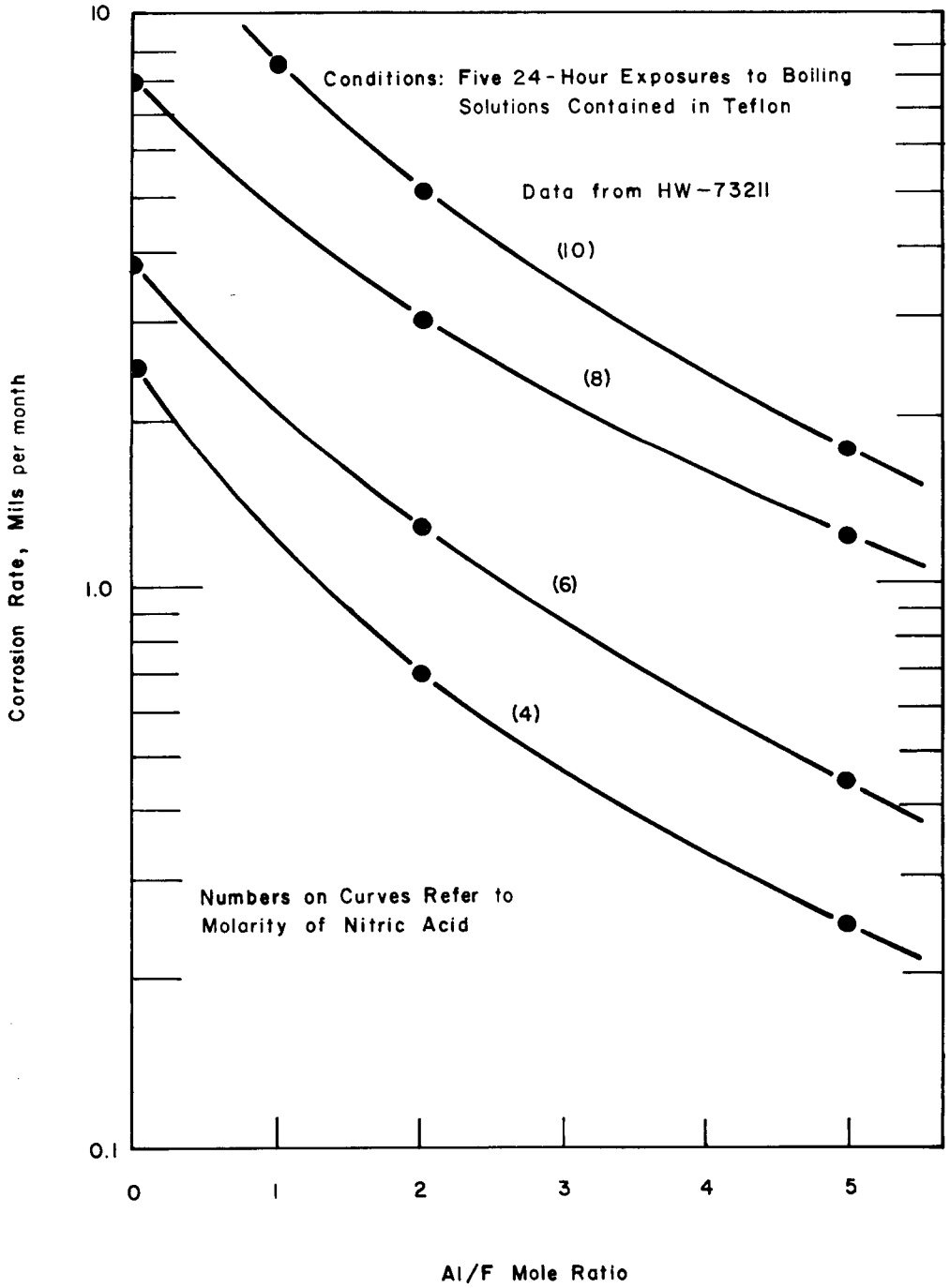

Fig. 10. Type 304L Corrosion Rates, 0.01*M* HF - HNO_3 - $Al(NO_3)_3$ System[35]

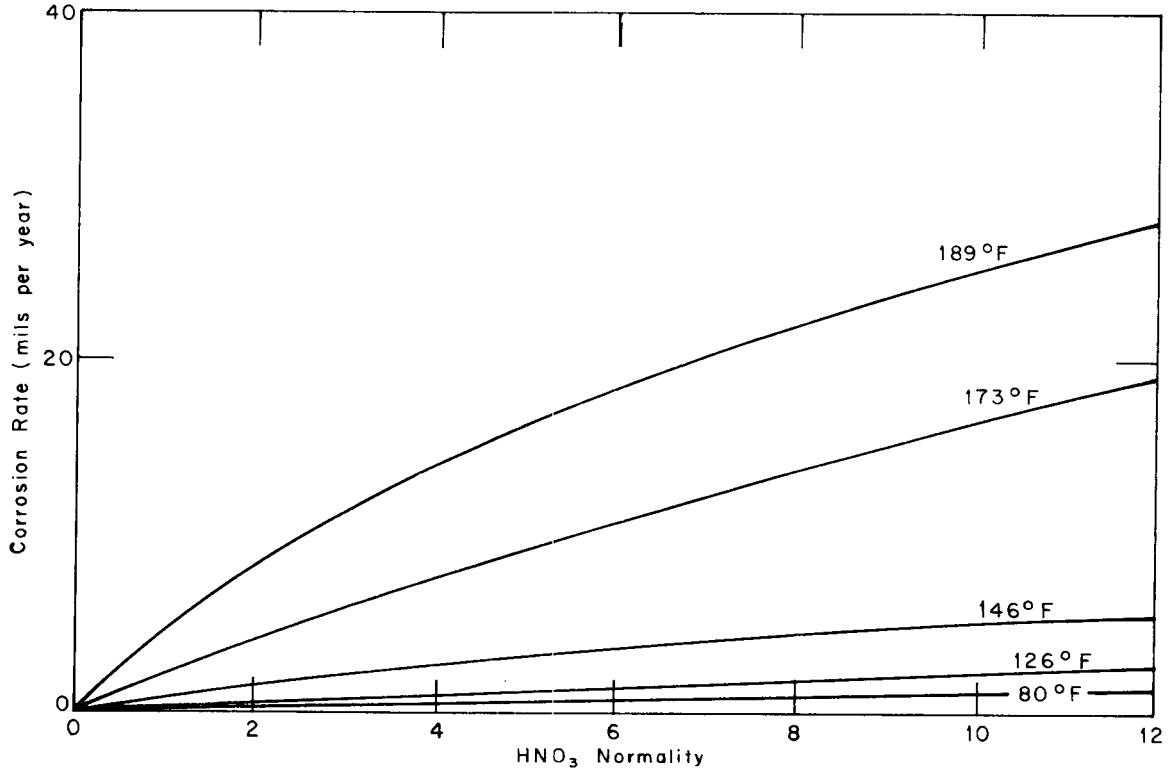

Fig. 11. Effect of Aluminum Addition on the Corrosion Rate of Type 304L Stainless Steel ($0.1M$ Al^{+3}, $0.1M$ HF, Al/F = 1.0)[36]

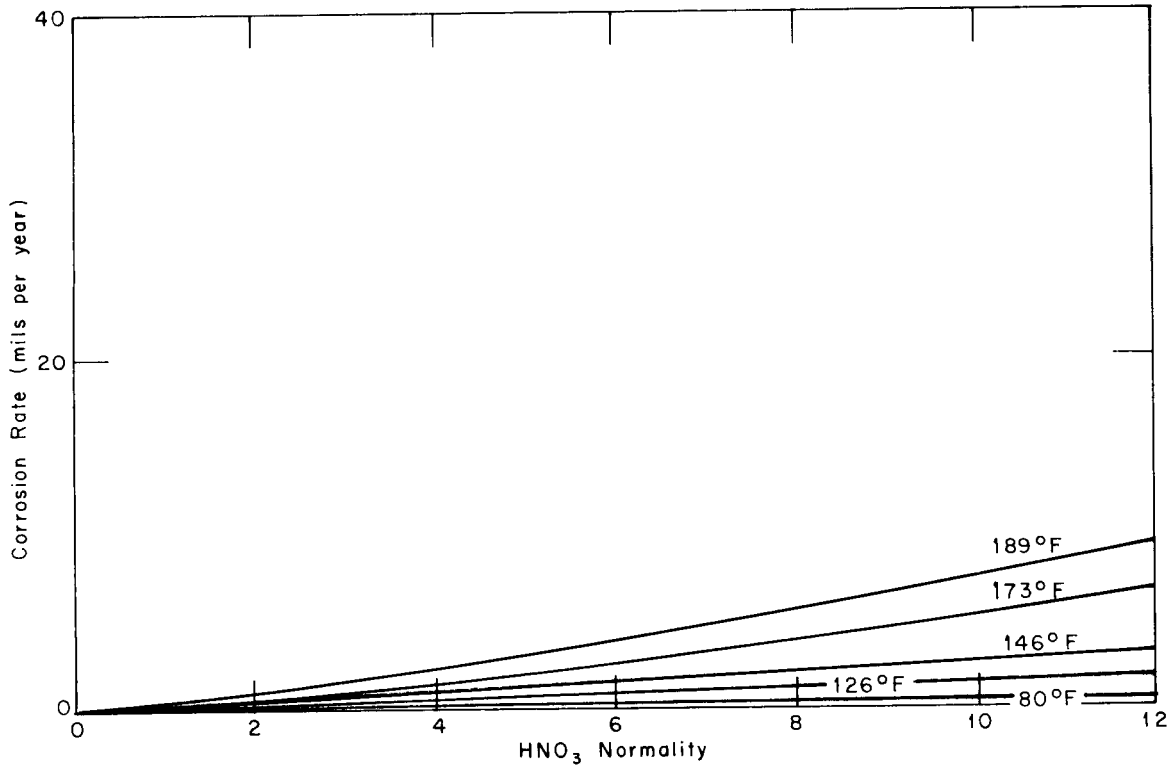

Fig. 12. Effect of Aluminum Addition on the Corrosion Rate of Type 304L Stainless Steel (0.2*M* Al^{+3}, 0.1*M* HF, Al/F = 2.0)[12]

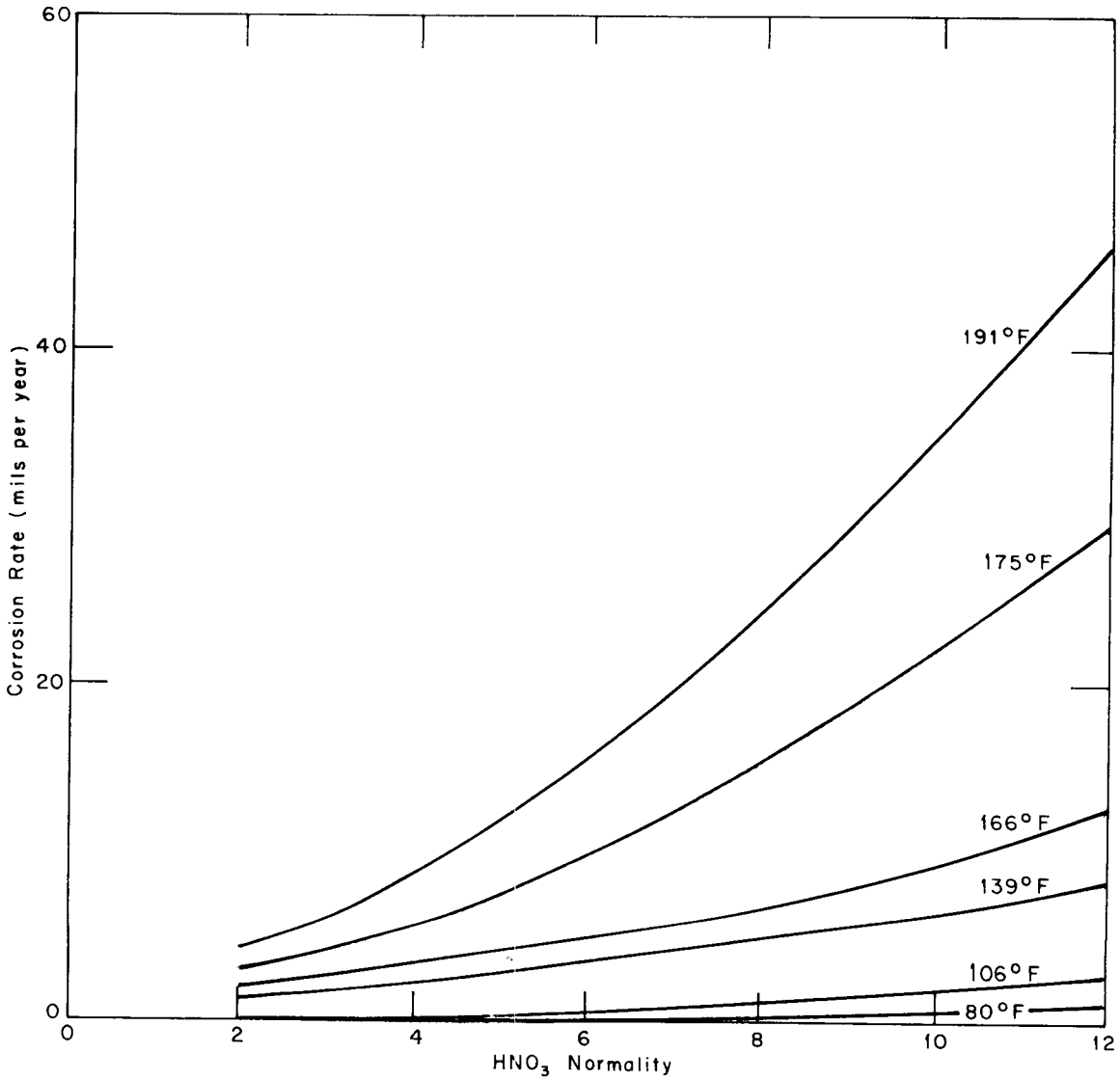

Fig. 13. Effect of Thorium Addition on the Corrosion Rate of Type 304L Stainless Steel (0.1*M* Th^{+4}, 0.1*M* HF, Th/F = 1.0)[13]

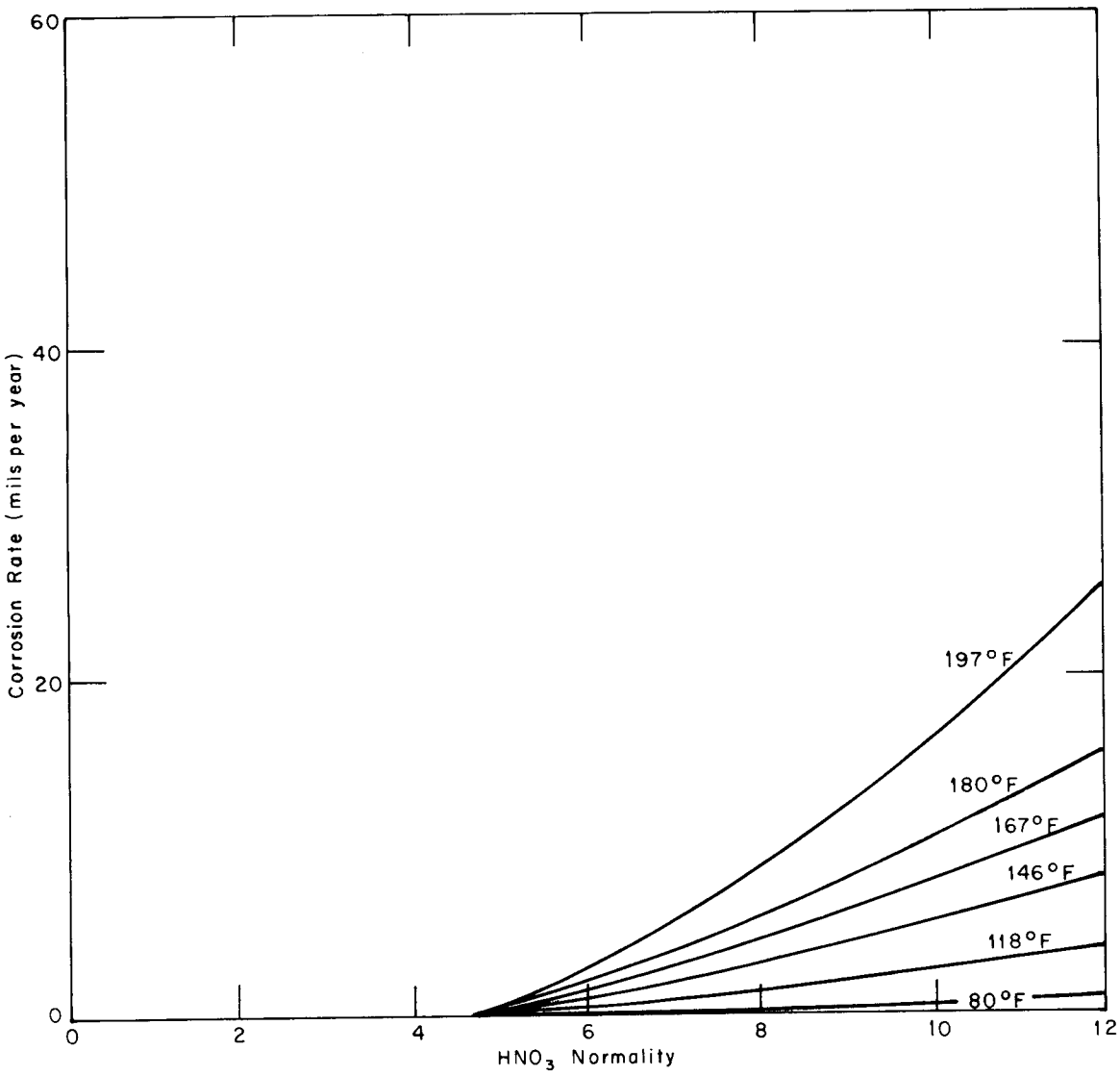

Fig. 14. Effect of Thorium Addition on the Corrosion Rate of Type 304L Stainless Steel (0.2*M* Th^{+4}, 0.1*M* HF, Th/F = 2.0)[14]

TABLE XVI
CORROSION OF WROUGHT TYPE 309SCb STAINLESS STEEL BY BOILING HNO_3 - HF SOLUTIONS[38]

Solution Composition, *M*			Liquid Corrosion Rate, mils/yr
HNO_3	HF	Zr^{4+}	
1.0	0.4	0	77
1.0	1.0	0.15	52
1.0	2.0	0.40	57
1.0	3.0	0.65	43

Miller, *et al*, announced that the reduced corrosion in a solution of 13*M* HNO_3 and 0.1*M* HF as a result of the addition of 0.1*M* $Al(NO_3)_3$ had been demonstrated[39]. The corrosion rates on Type 309SCb ss, as well as on a number of specialty metals, are one-fourth to one-eighth of those in the solution which did not contain the aluminum nitrate. The attack on the welds was also decidedly less in the inhibited solution.

6. Direct Correlation of Corrosion with Uncomplexed Fluoride

Mirolyubov, Zhuk, and Kurtepov in 1962, like others mentioned previously[12], found that the "addition of fluorides to nitric acid solutions leads to an increase in the rate of corrosion of stainless steels, the effect being specially marked at the boiling point of the solutions" and the "increase in the fluoride concentration causes an increase in the corrosion rate, which is greater the greater the nitric acid concentration"[40]. However, for a given concentration of fluoride a maximum is obtained, after which the rate diminishes slowly. Figure 15 shows this effect with varying concentrations of NH_4F, at given quantities of HNO_3. The maximum corrosion rate is shifted in the direction of lower nitric acid concentrations with increased fluoride concentrations and temperature. In the more concentrated solutions, the corrosion rate becomes especially sensitive to the temperature.

Mirolyubov, *et al*, were able to correlate corrosion rate with concentration of un-ionized hydrofluoric acid in the solution. Thus, the increase in corrosion of the steel by addition of fluoride ion to the nitric acid is determined by the concentration of the undissociated hydrofluoric acid. This, in turn, is determined by the hydrogen ion concentration and the concentration of ions which complex fluoride in the solution.

Recent measurements[41,42,43] of the stability of the fluoride complexes of aluminum, zirconium, and other elements, have made it possible to estimate the fluoride ion concentration or un-ionized HF concentration of complicated solutions and to predict corrosion properties.

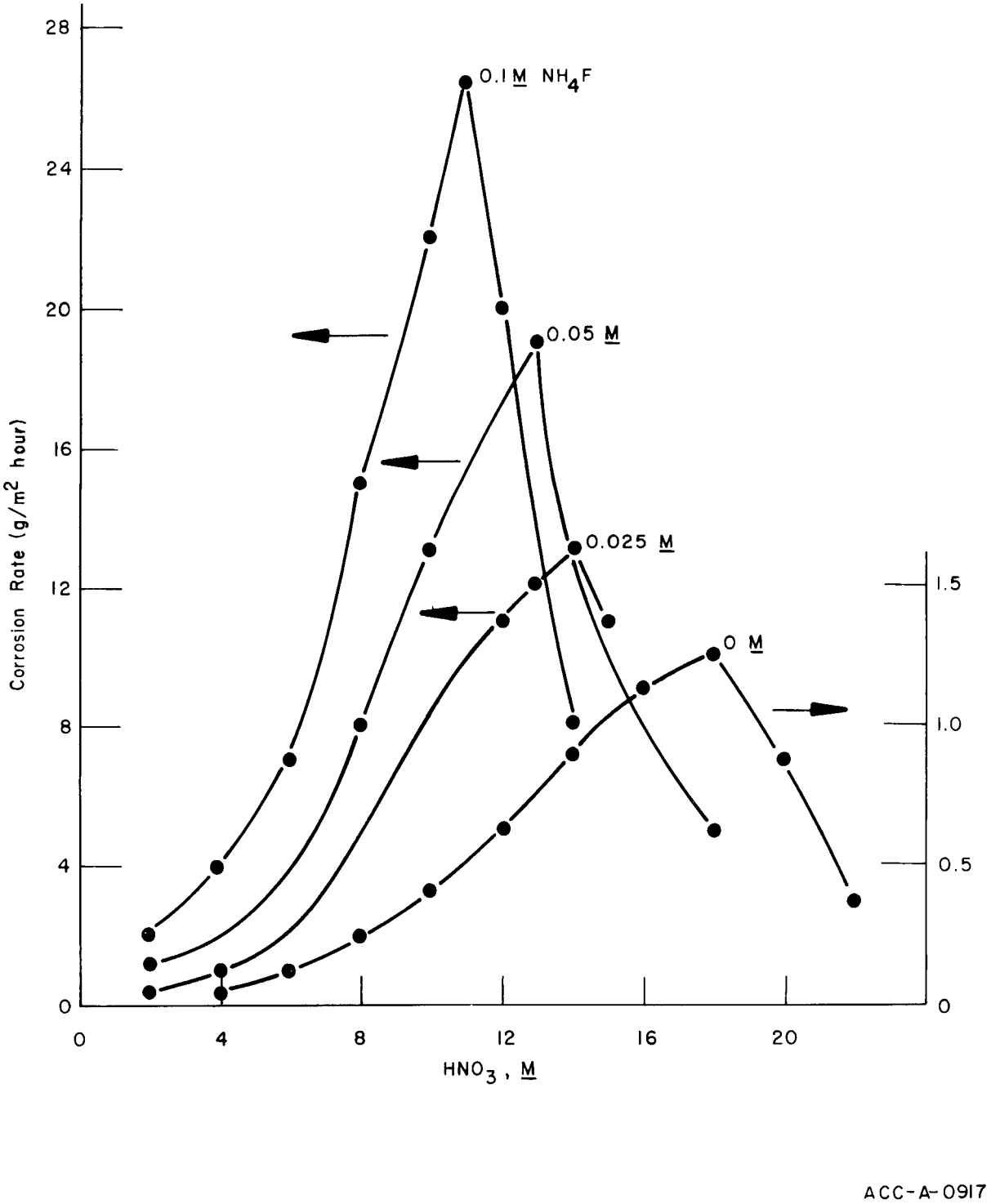

Fig. 15. Rate of Corrosion of Stainless Steel Relative to Boiling HNO_3 with Varying Concentrations of NH_4F

IV. CORROSION TESTS COMPLETED RECENTLY AT THE ICPP

Four alloys were evaluated recently at the ICPP for corrosion resistance to solutions containing nitrates and fluorides; they were: (1) unalloyed Type 304L ss, (2) Type 304 ss alloyed with 1.5% boron, (3) Type 304L ss alloyed with 0.3% boron, and Type 304L ss alloyed with 0.3% gadolinium (Table I). Additionally, the Type 304 ss alloyed with 1.5% boron was tested in complexed solutions. Aluminum, as aluminum nitrate, and zirconium metal as a sacrificial metal for the preferential attack of the fluorides, was used to furnish the complexing of the fluorides in the solutions. The solutions contained a range of components: 0.003*M* to 6.0*M* fluoride, 0.24*M* to 4.56*M* nitrate, 300 g/l uranium, up to 0.12 g/l boron, and 1.0*M* to 2.0*M* acidity.

While the solutions and corrosion results were too diverse to specify here, in general the results obtained indicated:

(1) Unacceptably high corrosion rates were indicated for the 1.5% boron-alloyed specimens while the 0.3% gadolinium-alloyed specimens were almost as good as the Type 304L ss.

(2) Tests with the 1.5% boron-alloyed steel where zirconium was added as a sacrificial metal for preferential attack had values only slightly higher than those for the gadolinium-alloyed metal.

(3) Complexing the fluorides in the solutions with an excess of aluminum was slightly more effective than the use of a sacrificial metal; however, in some cases solution stability problems were encountered.

(4) The rates for the 0.3% boron alloy were in the same range as for the 0.3% gadolinium alloy, or for the 1.5% boron alloy when a sacrificial coupon was present.

(5) It was empirically shown that corrosion of a given alloy varies directly with the calculated quantity of uncomplexed hydrofluoric acid present.

(6) Vapor phase corrosion is much less significant than liquid phase.

(7) Corrosion at 50°C is much greater than at ambient.

(8) Dilute solutions had lower corrosion than concentrated.

(9) Corrosion decreased as aluminum complexing of the solution increased.

V. CONCLUSIONS

The conclusions reached from this literature survey and corrosion study are:

(1) Type 304L stainless steel appears to be a suitable choice for service at the ICPP where the alloy will be in contact with fully complexed nitrate-fluoride bearing solutions. Other alloys containing even higher quantities of chromium and nickel might also have suitable or improved corrosion properties for this service.

(2) The proper annealing of stainless steels will improve their corrosion resistance.

(3) Where annealing is difficult or impossible, the choice of stainless steels stabilized with columbium or titanium will diminish weld-etch corrosion problems.

(4) The choice of stainless steels containing low carbon will also moderate corrosion problems.

(5) Where it is necessary to alloy neutron absorbing elements in the metal for criticality control purposes, their percentage should be kept to a minimum, as the corrosion rate increases with increasing concentration.

(6) Complexing nitrate-fluoride-containing-solutions with aluminum, zirconium, or thorium will also reduce corrosive effects.

(7) The corrosion of several stainless steel alloys has been shown to vary directly with the quantity of uncomplexed hydrofluoric acid present.

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